Argonne National Laboratory

GUIDELINES FOR SODIUM FIRE PREVENTION,
DETECTION, AND CONTROL:

Report of the Ad Hoc Committee on Sodium Fires

by

D. W. Cissel, L. F. Coleman,F. O. Pancner, F. A. Smith,and A. D. Tevebaugh

When you no longer need this report, please return it to TECHNICAL PUBLICATION BLDG. 2 The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U.S. Atomic Energy Commission, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona
Carnegie-Mellon University
Case Western Reserve University
The University of Chicago
University of Cincinnati
Illinois Institute of Technology
University of Illinois
Indiana University
Iowa State University
The University of Iowa

Kansas State University
The University of Kansas
Loyola University
Marquette University
Michigan State University
The University of Michigan
University of Missouri
Northwestern University
University of Notre Dame

The Ohio State University
Ohio University
The Pennsylvania State University
Purdue University
Saint Louis University
Southern Illinois University
The University of Texas at Austin
Washington University
Wayne State University
The University of Wisconsin

NOTICE-

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3,00; Microfiche \$0.65

ARGONNE NATIONAL LABORATORY 9700 South Cass Avenue Argonne, Illinois 60439

GUIDELINES FOR SODIUM FIRE PREVENTION, DETECTION, AND CONTROL:

Report of the Ad Hoc Committee on Sodium Fires

by

D. W. Cissel, L. F. Coleman, F. O. Pancner, F. A. Smith, and A. D. Tevebaugh

June 1970

DISCLAIMER NOTICE

Any comparison of the design or performance characteristics of manufacturers' products is not to be construed as an endorsement of one product over another. Stated preferences for a particular design or set of performance characteristics are intended solely to establish minimum acceptable specifications for a particular type of product when used in applications described herein. Any future procurement of products referred to herein by the AEC or its contractors, will be based upon normal competitive procedures. The procuring organization will in all instances specify the minimum specifications required.

PREFACE

This report is a modified version of a report prepared August 7, 1969, by an ANL Ad Hoc Committee established to evaluate, and to make recommendations concerning, the potential fire hazardassociated with various ANL sodium facilities. Since the original report was written, significant upgrading has occurred in the type and number of safety features of the sodium facilities at the Illinois and EBR-II sites. This "upgrading" is not reflected in the sections of this report that refer to these facilities (for example, the section on sodium leak detectors used at ANL).

Mr. L. E. Oldendorf (AEC-CH Safety and Technical Services Division) requested that the Committee's original report be modified into a form suitable for general distribution.

TABLE OF CONTENTS

			Page		
ABS	ABSTRACT				
I.	INT	TRODUCTION	9		
II.	SO	DIUM-SYSTEM LEAK DETECTION AND EXPERIENCE	10		
	A.	Sodium-leakage Incidents	10		
		 ANL Core Component Test Loop (Illinois Site) Hallam Nuclear Power Facility (HNPF) 	11 11		
	в.	Leak-detection Methods	12		
		1. Idaho Facilities	13 14		
	C.	Use of Leak Detectors	15		
III.	SO	DIUM FIRE DETECTION	15		
	A.	Visual and Olfactory Detection	16		
	B.	Television Monitors	16		
	C.	Electronic Smoke Detectors	17		
	D.	Flame Photometer	18		
	E.	Atomic-absorption Detector	18		
	F.	Light-emission Detector	18		
	G.	Light-absorption Detector	19		
	н.	Conductivity and pH Detectors	19		
	Ι	Secondary-type Detectors	19		
IV.	SO	DIUM FIREFIGHTING	20		
	A.	Possible Sodium-fire Situations	21		
		1. Inert-atmosphere Enclosure	22		
		 Reasonably Gas-tight Enclosure, Air Filled Air-filled Semienclosure That Can Be Converted 	22		
		to Complete Enclosure	23		
		to a Specific Area	23		

TABLE OF CONTENTS

		<u> </u>	age
		5. Sodium or NaK Spills in Open Areas6. Sodium or NaK Drippage or Sprays from Elevated	26
			26
		8. Sodium or NaK Fires in Regions with High Radiation	27
		Backgrounds	27
	в.	Effects of Alkali-metal Oxide	28
v.	GE		29
	A.	Effectiveness of Sodium Firefighting Methods	29
	В.	Need for Research and Development on Extinguishing Agents and on Extinguishment of Large Sodium Fires	30
	C.	Visibility, a Major Handicap	31
	D.	Use of Drip Pans with Perforated Plates	31
	E.	Sodium-fire Detection Problem	32
	F.	Design of Total Enclosures	32
	G.	The Need for Additional Research and Development on Materials	33
AP	PEN	NDIXES	
	A.	Sodium Facilities Survey	34
	в.	Sodium Leak and Fire Detection and MET-L-X Systems	36
		1. Sodium Leakage Detection: State-of-the-Art Study, LMEC-Memo-69-35	36
		2. An Examination of Some Methods for Detecting Liquid Metal Leaks in D.F.R. Secondary Heat Exchangers	73
		3. Extinguishing Agents for Metal Fires	87
		a. Ansul Extinguishing Agents for Combustible Metal Fires	87 89
		for Metal Fires	90

TABLE OF CONTENTS

C. Liquid-metal Fires and Scrubber Systems	9
J. J. Droher (69LMEC-686), General Information and List of Films on Liquid-metal Fires and of Reported	
Accidental Sodium Fires 90	8
2. Film: Sodium Expulsion into Air 108	
3. Summary of Information on Sodium Fires and on Sodium or Plutonium Aerosols as They Pertain to Sodium Fires	9
4. A Study of Sodium Fires, J. D. Gracie and J. J. Droher, NAA-SR-4383 (summary only)	8
5. Extinguishment of Alkali Metal Fires, S. J. Rodgers and W. A. Everson, Fire Research Abstracts and Reviews, 8(1), 40-41 (1966)	3
6. Additional References for Appendix C 125	5
D. Tabular Listing of Known Equipment or Component Failures in Sodium Loops or Reactors	6
E. Safe Handling of Alkali Metals	9
1. A Primer for the Safe Use of Liquid Alkali Metals, Frank A. Anderson, ORNL-TM-1740	9
Methods Used by an AEC Contractor for Handling Sodium, NaK and Lithium	5
3. Explosions Involving Metallic Potassium or NaK 150	9
4. Additional References for Appendix E 164	4
ACKNOWLEDGMENTS	5
REFERENCES	6

LIST OF FIGURES

No.	Title	Page
1.	CCTL Valve and Flange Damaged by Small Sodium Leak	11
2.	Van Stone Flange in CCTL Damaged by Sodium Leak	11
3.	Damage to the Exterior of a Hallam Sodium-expansion Tank (~5-ft diameter, Type 405 stainless steel) after a Sodium Leak	12
4.	View of Damage in the Area of the Nozzle (8-in. diameter) to Tank Weldment (leak area)	12

GUIDELINES FOR SODIUM FIRE PREVENTION, DETECTION, AND CONTROL:

Report of the Ad Hoc Committee on Sodium Fires

by

D. W. Cissel, L. F. Coleman, F. O. Pancner, F. A. Smith, and A. D. Tevebaugh

ABSTRACT

The problems of sodium-fire prevention, detection, and fighting are discussed, and recommendations are presented. Some pertinent literature articles are reproduced in the appendix sections.

I. INTRODUCTION

An ANL Ad Hoc Committee on Sodium Fires was formed on April 25, 1969, by a memorandum from Dr. R. B. Duffield, Laboratory Director, to members of the Committee. The directed objectives of the Committee were as follows:

- To classify the various operations at the Laboratory using sodium in quantities large enough to constitute a significant fire hazard.
- To evaluate the effectiveness of the various ways of putting out out sodium fires.
- To recommend methods of handling sodium fires which should be considered for use in the various classes of sodium operations.

At an early stage in its studies, the Committee concluded that highly effective methods of extinguishing sodium or NaK fires of all types did not exist and that, therefore, appreciable emphasis should be placed on preventing such fires, limiting their spread, and detecting them at an early stage.

The Committee contacted several AEC installations, including AEC-CH Safety and Technical Services Division and the Liquid Metal Engineering Center (LMEC), for information on sodium fires and related subjects. From

these and other sources, the Committee amassed a large body of reports, most of which were reviewed. The more pertinent references (including a reference to motion pictures on the extinguishing of alkali-metal fires) are listed in this report, along with a few of the most relevant reports themselves. The Committee also observed tests (conducted by the ANL Fire Protection Department personnel) of old and new designs of sodium-fire smoke detectors.

Survey sheets describing the various ANL alkali-metal facilities were prepared, and an example of one of these sheets is in Appendix A. These sheets described the type of work, quantities of alkali metals, equipment construction and operating conditions, fire detection and safety measures, and potential fire hazards. This descriptive information concerning the various ANL alkali-metal facilities and the Committee's conclusions and recommendations concerning these facilities are not included in this report.

II. SODIUM-SYSTEM LEAK DETECTION AND EXPERIENCE

The construction of most sodium systems enhances the possibility that small leaks may develop that do not immediately give indications of a fire. Small leaks behind pipe insulation, within valve bonnets, and from systems within inert enclosures are some examples of this type of leak. Eventually, the leak may progress to a state where its presence can be detected by fire-detection methods described in Section III. In some cases, however, the consequences of delaying detection until this later stage can be very serious; therefore, special leak-detection methods are necessary.

Hot sodium air reaction products (oxide, peroxide, hydroxide, etc.) cause rapid deterioration of austenitic steels and other metals or alloys used for sodium systems. Thus, in the presence of air, sodium from an initially small leak will create a very serious corrosion condition on the exterior surface of a metallic system. Similarly, flanges and flange bolts may also be seriously eroded by sodium from a small leak. Small leaks can rapidly become large leaks, the rate of growth of the leak depending on the original leak size, details of the container (such as thickness), system pressure, temperature, and the availability of oxygen and probably moisture. The early detection of small leaks is, therefore, very important in minimizing the consequences of the leak. If a leak can be detected while it is still small, system pressure can be reduced and the sodium can be drained from the vicinity of the leak or it can be frozen; therefore, damage to the facility can be held to a minimum.

A. Sodium-leakage Incidents

Examples of cases in which small leaks resulted in extensive system failures cannot be given because such failures destroy evidence of

the initiating cause. Two examples are available, however, of small leaks creating situations bordering on extensive failure; these examples exemplify the need for early detection of small leaks. A brief description of these two cases follows.

1. ANL Core Component Test Loop (Illinois Site)

A small leak was detected in the ANL Core Component Test Loop (CCTL) by operator observation of smoke. Subsequent observations showed that a small leak had developed in either a valve bonnet-to-body flange or nearby in the connecting 2-in. piping. The sodium and its airreaction products were trapped by the pipe and valve insulation and severely attacked the contacted exterior surfaces of the valve and connecting piping (see Fig. 1). The attack upon the Van Stone flange (see Fig. 2) used to connect the valve bonnet to the flanged valve body was particularly severe, almost destroying the integrity of this connection. Had this flanged joint failed under the 50-psig system pressure, the entire loop inventory of 900 gal of 1150°F sodium would probably have been discharged into the pit housing the loop. The loop pump delivers 400 gal/min of sodium and has about a 2-min inertial coastdown time. The prompt action of the loop operators at the onset of visible smoke from the CCTL facility was to turn the pump off and to drain the loop into a dump tank. The valve did not completely fail; damage therefore was limited to loss of the valve and several feet of pipe.



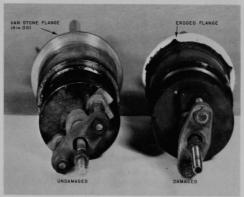


Fig. 1. CCTL Valve and Flange Damaged by Small Sodium Leak

Fig. 2. Van Stone Flange in CCTL Damaged by Sodium Leak

2. Hallam Nuclear Power Facility (HNPF)

At the Hallam Nuclear Power Facility, a 5-ft-diam expansion tank (Type 405 stainless steel) in a secondary sodium loop developed a

leak at a nozzle-to-tank weldment (8-in.-diam nozzle). The vessel was contained in a well-insulated, sheet-metal-clad jacket. The leak was discovered by operating personnel who observed sodium oxide in the air, and a small amount of sodium was found to be leaking through the aluminum jacket surrounding the pipe insulation. The system was secured and the sodium was drained. The mechanical sheet-metal jacket and the insulation were removed. Examination of the exterior vessel wall showed that severe corrosion had occurred with penetrations as deep as half the thickness of the wall. Subsequent metallurgical analysis indicated that the initial leak was probably a small "weeper." The damage to the expansion tank wall (see Figs. 3 and 4*) was so extensive that repair was not considered feasible and the tank was replaced.



Fig. 3. Damage to the Exterior of a Hallam Sodiumexpansion Tank (~5-ft diameter, Type 405 stainless steel) after a Sodium Leak



Fig. 4. View of Damage in the Area of the Nozzle
(8-in. diameter) to Tank Weldment (leak
area)

B. Leak-detection Methods

Many potential and proven methods of early leak detection are described in the literature. The 1967 draft version of the "Liquid Metals Handbook, Sodium and NaK Supplement" includes a brief survey of leak-detection methods. The general methods listed in the Supplement as applicable to detection of leakage of liquid metal from the system and of air or water into the system are:

^{*}Figures provided by J. D. Stearns, Atomics International.

- 1. Visual observation, including television methods.
- 2. Electrical conductance -- "shorting" of wires or probes.
- 3. Volume change--applicable only to small-volume systems.
- 4. Third-fluid-monitoring of compositions, pressure, etc. of an intermediate fluid between the liquid-metal system and the water system in liquid-metal-to-water heat exchangers.
- Impurity detectors--detection of reaction products in the system in case of air or water inleakage.
- Cover-gas pressure--detection of pressure increase due to hydrogen formation in case of water inleakage.

The first two methods are those most frequently used except for a few, but very important, cases involving sodium-to-water heat exchangers or water-cooled liquid-metal pumps, where methods 4, 5, and 6 are also used. Continuous hydrogen-gas chromatography can be used to monitor for leaks between sodium and water systems. Optical and ionization types of smoke detectors are frequently used to detect sodium fires, and literature data indicate that spectroscopic methods (emission and absorption) are capable of detecting ppm quantities of sodium or sodium oxide.

The Liquid Metals Engineering Center (Atomics International, Division of North American Rockwell Corporation) has conducted a study on the state-of-the-art in sodium leak detection; the results of this study are summarized in report LMEC Memo 69-35, which is included in Appendix B. A brief but useful survey of some potential methods of leak detection and a comparison of their potential advantages and disadvantages are given in a British report (UKAEA, unpublished paper by Smith and Drummond), which is also included in Appendix B.

Many sodium leak detectors of various types are used in ANL sodium facilities. Discussion of the types used is best served by considering facilities at Idaho and at Illinois separately.

1. Idaho Facilities

The major sodium facilities at Idaho are those associated with EBR-II. The electrical-conductance leak detectors used in these facilities are of the probe (or spark-plug) type. They are simple in construction and operation. The probes used at EBR-II consist of two conductors spaced 1/16 to 1/4 in. apart, shorted together by leaked sodium, or a single conductor, shorted to ground by a leak. A relay coil is in a parallel circuit with the probe and remains energized unless a leak occurs. Shorting of the probe deenergizes the relay. Alarm or control action is obtained through use of the relay contacts. The probe circuits are routinely checked using a

shorting switch, and the system is checked (at least semiannually) by shorting the probes. Because of the simplicity of the detector, few false alarms have been received. These simple detectors have successfully indicated leaks in the main secondary sodium pump, the secondary sodium system rupture-disc assemblies, and a number of small valve bellows.

In the primary EBR-II sodium system, probes are installed to monitor for leakage in the primary tank annulus, the primary purification electromagnet (EM) pump, Conoseal pipe fittings and the drip pan in the cold-trap vault, and valve bellows in the purification and sampling systems.

In the secondary sodium system, probes are installed to monitor for leakage in the rupture-disc assemblies, the main EM pump, the two recirculating EM pumps, and about 20 valve bellows.

In the evaporators and superheaters of the secondary sodium system, a sodium leak through the weld between the outer duplex tube and the sodium tube sheet could be detected by visual observation of smoke in the air space between the sodium and water-tube sheets. The inter-sheet space on each unit is inspected regularly by operators for indication of sodium leakage.

In the evaporators and superheaters, a leak that penetrated a duplex tube would permit water or steam to enter and react with the sodium. A continuous gas chromatograph monitors the hydrogen in the secondary cover gas. A continuing increase in hydrogen concentration might indicate a water-to-sodium leak. Such an observation would indicate the probable need for plant shutdown and sodium drainage before serious damage occurred.

2. Illinois Facilities

The sodium facilities at Illinois differ significantly from those at Idaho in size and permanency. Sodium systems at Illinois are usually small, involving less than 100 gal of sodium, and are of an experimental nature; they therefore may have unmodified lives of only months or a very few years. The sodium systems at Idaho involve thousands of gallons of sodium (90,000 gal in primary and 17,000 gal in EBR-II secondary system) and are of a permanent nature with periodic upgrading.

The small size of each Illinois sodium facility, with the possible exception of the CCTL, and the absence of significant radioactivity permit close and frequent approach to the facility. Primarily because of this, the most widely used methods of leak detection at Illinois sodium facilities are visual and olfactory. Smoke detectors are installed in systems where sodium is pumped.

Simple spark plugs are often used as conductance devices to monitor the integrity of specific components, particularly bellows-sealed valves. The plug is screwed into the space between the primary seal (bellows) and the secondary stem seal (conventional packing). Pressure gauges have also been used to monitor for leakage into this inner-seal space.

Single and duplex-insulated wires have been wrapped around sodium process piping to detect leaks. The value of such a detection device has not been proven because leaks did not develop in the systems where the wire-wrap detectors were used. Leaks have, however, been detected by failure of heater calrods and heater wires used with piping and equipment.

c. Use of Leak Detectors

The need for leak detection in sodium systems is apparent. Ideally, leak detection should be provided on all components in a system, but the complexity of such an application requires a compromise based upon economics. Facilities of great value, or those in which fires could cause appreciable financial loss, should have extensive leak-detection systems with remote annunciation of a leak. Conversely, small experimental facilities can scarcely justify a complete leak-detection system, and these facilities must operate with a far less extensive system.

To estimate the most probable sources of leaks in sodium and NaK systems, a survey was made of readily available descriptions of system failures; the data collected in this survey are given in Appendix D. The survey showed the overwhelming predominance of bellows failures. This susceptibility to failure indicates that a bellows used in a sodium system should always be accompanied by an associated leak-detection system. Leak detectors should be used for all bellows applications including valves, rod seals, and expansion and misalignment devices. This precaution should be extended to other equipment components where high stresses occur repetitively.

III. SODIUM FIRE DETECTION

Sodium and NaK systems should be conservatively designed and fabricated, and then tested to ascertain that the probability of a fire during subsequent operations is very small. Despite these precautions, the possibility of a fire always exists. If a sodium or NaK fire occurs, the damage can be minimized if the fire is detected at an early stage and corrective measures taken.

Many methods have been suggested in the literature for sodium fire detection. A number of these methods are described and evaluated in an unpublished paper by Smith and Drummond (see Appendix B). A few of the

methods described in the literature²⁻⁶ (e.g., flame photometry and spectroscopic methods) are very sensitive and show promise for being developed into commercial devices.

The methods most commonly used for fire detection are discussed below, and a few methods showing promise for commercial development are also described.

A. Visual and Olfactory Detection

Visual and olfactory identification of the dense oxide smoke formed when alkali metals burn are sensitive and common methods used for fire detection. Because the commercially available automatic detectors are much less sensitive, the operators of even large, expensive alkali-metal systems rely heavily upon the visual detection of a fire.

There are many examples of a sodium fire being detected visually long before an automatic alarm functioned. For example, a fire in the EBR-II primary sodium-purification cell was first detected by a plant operator. The building smoke detectors (none were located, however, in the cell since they were installed primarily to detect electrical fires) and ventilation exhaust radioactivity monitors* did not detect the fire. The nonradioactive-sodium fire at the Core Component Test Loop (CCTL, ANL Illinois Site) was also first detected visually, and the commercial ionization detector located within the loop enclosure failed to detect the fire. The ionization detector, however, was in a poor location relative to the location of the fire (a fire does not always occur near a detector, and frequently equipment changes occur without considering the possible need for relocating the fire detectors), and the detector was not as sensitive as some newer detector designs available on the market.

Visual fire detection demands that personnel are within view of the sodium fire, and the complexity of a reactor plant like EBR-II and the inaccessibility of totally enclosed experiments precludes the possibility that all sodium fires will be visually detected in time to prevent significant plant damage. For this reason, automatic detectors must be relied upon.

B. Television Monitors

A modification of visual fire detection is the use of closed-circuit television. At the ANL Illinois Site, such a system is used by a two-man off-shift crew to monitor sodium operation between Buildings 206 and 308. In this application, the two-man shift is required at only one building. The TV monitor can be used by men at either site to monitor unattended

^{*}Sodium activity was below normal levels since the reactor had been shut down five days before the incident.

sodium operation at the other site. The use of a TV monitor to view one or more remote locations demands, however, that an operator watch the monitor!

ANL has experienced practical problems in the maintenance of the TV monitor. For example, a TV monitor, in itself, can give more operational problems than the sodium system that the monitor is supposed to view. In addition, a single TV monitor has a limited field of view. A monitor focused to observe one small area in great detail cannot view a large area at the same time. Conversely, a monitor focused to give a very wide field of view may not detect a small fire until the small fire has become large.

C. Electronic Smoke Detectors

Ionization-type smoke detectors from commercial suppliers have been used to detect liquid-metal fires. These detectors use an alphaemission source (americium oxide or radium sulphate of 20-130 μCi) with an appropriate electronic circuit to measure a change in ionization current due to a fire (sodium oxide) and to trip an alarm circuit. This type of fire or smoke detection is used at ANL liquid-metal facilities at Idaho and Illinois and by other liquid-metal facilities such as FERMI and the large test loop at Atomics International. Ionization-type smoke detectors are generally used on installations with cells or rooms where continuous visual access is not practical or feasible, where use of TV may also be impractical or uneconomical, and where some ability to detect a sodium fire is required. An isolated sodium storage tank area of a reactor complex, which has a low probability of personnel access, is one example of the type of building area where one would use an ionization-type smoke detector.

Commercial ionization detectors require routine maintenance and calibration. They are relatively insensitive to sodium oxide smoke (smoke densities that are readily detected visually may not actuate the ionization detector). The detectors should be located very near the potential fire site and must be in the ventilation airflow in order that the time delay in detecting the fire be a minimum. This may create a problem in large spaces where there is no specific pattern of airflow, and actual location of a fire in a complicated or modified system may not coincide with the fire location predicted when the detector was installed. Furthermore, the ionization detector is quite sensitive to normal smoke and combustion gases (for example, from a welding torch), and this sensitivity often results in false alarms. Because of this problem, these detectors are frequently installed in a compromise location, or the sensitivity of the detector is reduced to a point that its value as a sodium fire detector is severely limited.

An improved type of photoelectric fire detector (one design is interchangeable with the ionization type) is now commercially available, and this instrument does not appear to have some of the disadvantages of the ionization-type detector. In the photoelectric detector, smoke particles entering the chamber are illuminated, and the scattered light from these particles reaches the photocell, causing an alarm. These detectors are recommended by the manufacturers of both ionization and photoelectric fire detectors for applications in which it is not practical to use ionization detectors due to high ambient concentrations of combustion products (welding areas, etc.), and in which the material expected to burn produces a dense visible smoke. Preliminary tests by the ANL Fire Protection Department indicate that the photoelectric detector has much greater sensitivity to sodium oxide smoke than the ionization detector and is recommended for installations where sodium or other smoke-producing metals might be the prevalent type of fire; however, the location of the photoelectric detector must also be selected with care.

D. Flame Photometer

Flame-photometric methods are widely used in analytical chemistry laboratories to measure small amounts of metal ions. The method is very sensitive for sodium ions, which can be excited in a relatively low-temperature flame; the intensity of the emitted light (a wavelength specific for sodium) can be measured by using filters and a photocell. The flame photometer, in principle, should be much more sensitive than an ionization detector, and a flame photometer can be made specific for sodium ions.

E. Atomic-absorption Detector

Atomic-absorption spectrometry has been used by Meyer and Young at the Oak Ridge National Laboratory to detect traces of NaK in air. The method is in essence the converse of flame photometry. A beam of light from a sodium lamp is passed through a flame, which consumes the air containing sodium or sodium oxide from a fire. The sodium light is absorbed by the nonexcited sodium atoms in the flame, and the attenuation of the light from the sodium lamp is a measure of the amount of sodium in the air. Meyer and Young report that 60 ppb of sodium in air can be detected by this method. The method is perhaps worthy of further study, but it does not appear to be as simple as, and may not be any more sensitive than, the flame-photometer detector.

F. Light-emission Detector

The brilliant light emitted by burning sodium could be detected by photocells or photomultiplier tubes in appropriate electronic circuits; suitable filters could make the device fairly specific for sodium light. This method would give an immediate signal when the sodium ignites; all other methods (other than visual) discussed in this report require that the sodium smoke be carried to the device (or to a collimated beam of light) in a circulating air stream. There apparently is insufficient data in the literature

(see unpublished paper by Smith and Drummond in Appendix B) for a critical evaluation of a light-emission detector; however, in principle, the device appears to be worthy of further consideration.

G. Light-absorption Detector

Burning sodium produces a dense opaque smoke; therefore, a collimated beam of light focused on a photocell should be a sensitive method for the detection of a sodium fire. The instrument would be simple and inexpensive, and has no moving parts. In regard to a device of this type, Smith and Drummond (see Appendix B) state: "Sensitivity has not been tested, but it is believed that the dense smoke from burning less than 1 g of sodium should be easily detectable." Difficulties, however, have been experienced with detectors of this type due to dust accumulation upon the light source and the photocell. These units are commercially available in the U.S., but they are infrequently used at ANL because of false-alarm and maintenance problems.

H. Conductivity and pH Detectors

Sodium oxide is readily soluble in water and would cause a marked change in the pH or conductivity of the water. This principle might be used in a detection device in the following way: A small fan would blow air past a cold condenser coil where the water condensate (from the air) would be collected continuously in a small receiver containing a pH electrode or a conductivity cell. A significant change in the pH or conductivity of the water would indicate the presence of sodium oxide in the air.

An unpublished paper by Smith and Drummond (see Appendix B) describes a limited study of a pH detector method, and the results were favorable for some types of applications.

I. Secondary-type Detectors

The preceding discussion was primarily concerned with methods or devices to detect a sodium fire by sensing conditions specific to sodium or its oxide. Such primary sensing devices must at times be replaced or supplemented by devices that are sensitive to more general conditions. To remotely detect fires involving radioactive sodium, it might be advisable to supplement smoke detectors with radioactivity monitors in a ventilation exhaust duct or shielded ventilation side loop. Smoke detectors for semienclosed sodium facilities might be supplemented with temperature detectors (e.g., rate-of-rise type) in the ventilation exhaust. Smoke detectors for totally enclosed, nonventilated sodium facilities might be supplemented with or replaced by pressure detectors.

There is no single method of fire detection that will serve all the widely varied applications. Many of the smaller sodium facilities can adequately be protected by visual observation combined with ionization or photoelectric smoke detectors. An important few of the facilities, however, will require different mechanisms for fire detection. Because of the importance of early fire detection in limiting the consequence of a sodium fire, the proper choice, location, and application of the fire detectors should be of as much concern to the sodium facility designer as in the integrity of the main facility components. The installation of fire detectors should receive a high priority; and when sodium equipment design changes occur, the fire detector's location should be reevaluated!

IV. SODIUM FIREFIGHTING

Sodium fires display several unique features that limit their control and extinguishment, and highly effective firefighting agents are not available for many sodium fire situations (see Appendix C). Conventional firefighting agents are normally useless. In general, fluids cannot be used for fighting such fires, because most fluids are either flammable or they react with sodium with explosive violence. Inorganic powders, almost alone, are the agents used for extinguishing sodium fires. The theoretical densities of these powders, however, are greater than the density of liquid sodium. This limitation upon firefighting fluids, and the fact that the inorganic powders, to prevent their sinking below the surface of the sodium, must be applied gently, severely limits the distance from which firefighting can be done. Sodium fires, particularly large or radioactive fires, can be very difficult to extinguish by manual firefighting methods; therefore, the use of sodium dump tanks, inerted enclosures, automatic fire-extinguishing systems, and conservative engineering design criteria should always receive careful consideration as fire-control methods. Firefighting experience to date has been limited to relatively small sodium fires, and very large sodium fires, under some conditions, may be essentially impossible to extinguish.

Molten sodium is extremely reactive with water or with materials containing adsorbed or loosely bound water. This extreme reactivity results in explosive spread of the fire when sodium contacts such conventional materials as concrete floors. Molten sodium can also reignite without external reignition sources. This feature requires the continuing attention of firefighting personnel for a period long after the fire has apparently been extinguished. This attention must also be continued during the final cleanup process after the fire.

Burning sodium produces a particularly obnoxious aerosol. It is an inhalation hazard to fire fighters and necessitates self-contained breathing apparatus. Its most obnoxious characteristic, however, is that it forms a dense cloud in the enclosure and severely limits or prohibits visibility of the

fire. The limited visibility and the limited range of the available extinguishing agents severely inhibit firefighting activities.

Plans for firefighting can only be formulated after considering two broad types of sodium fires. MacPherson⁸ states:

"Sodium fires can be subdivided into those fires characterized by combustion of a sodium pool and those due to a leak or rupture that produces a burning spray. A special case of the spray fire is one in which sodium is introduced explosively into an oxidizing atmosphere.

"Pool fires normally result from the accumulation of sodium on flat or recessed surfaces following either the rupture of sodium-containing equipment or the development of spray-producing leaks. The pool fire is characterized by a slower burning rate than that of the spray fire because of limited access of oxygen to the reaction zone. The rate of energy released is normally low and extremes of temperature and pressure do not develop in an enclosed volume containing such a fire.

"The spray fire has all the problems associated with the pool fire; however, the problems are compounded by the increased reaction rate which results from more intimate contact between the sodium and air. The rate of energy released in a spray fire is a function of the reactant temperatures, the spray energy or degree of dispersion, the humidity, the oxygen concentration, and the geometry of gas volume. The specific case of a spray fire that involves the explosive introduction of sodium is of particular concern because the extremes of temperature and pressure would be expected in this case."

Extinguishment of alkali-metal fires may be complicated by the characteristics of the leak such as elevation and force, characteristics of the resultant pool such as depth and confinement, proximity of other combustibles, and restrictions upon accessibility caused by radioactivity levels. With proper design and planning, any of these complications can generally be minimized to an extent that fire extinguishment is not a major problem, but if design and planning are inadequate for a particular situation, the consequences and difficulties in extinguishing a sodium fire can be extremely serious.

A. Possible Sodium-fire Situations

The interrelationship of the extinguishment complications and the design of an alkali-metal facility offers almost unlimited variations, but many of the salient features of the interrelationship can be discussed while

considering eight situations. The situations are arranged in decreasing order of ease of extinguishment of the alkali-metal fire.

1. Inert-atmosphere Enclosure

Alkali metals require oxygen (or other reactants) to start and maintain combustion; therefore a dependable enclosure containing an inert atmosphere is the ideal means to prevent alkali-metal fires. Unfortunately, this means is also expensive and presents a significant risk to personnel that have to enter the enclosure and therefore is probably restricted to cases in which the probability of metal leakage is high or the consequences of an alkali-metal fire are very serious.

Inert-atmosphere enclosures have been seriously considered for complex piping systems in advanced LMFBR designs and were used for the Hallam reactor. Similarly, most of the EBR-II primary sodium system is contained within the primary tank, which uses an inert cover gas. The French have used a unique version of inerted enclosure by containing a 5-MW sodium-heated steam generator inside a nitrogen-filled enclosure. In this case, although a sodium-water reaction is possible, explosion of the resultant hydrogen or a sodium fire is not possible due to the exclusion of oxygen.

When such protection is warranted, care must be taken to ascertain that the integrity of the enclosure will be maintained under accident conditions and that the atmosphere is sufficiently inert (a monitoring device should be provided); otherwise, the application will provide false security. In this regard, it is important to coordinate enclosure strength with pressure relief means to accommodate the pressure surge that may result if molten alkali metal is rapidly ejected into the enclosure.

2. Reasonably Gas-tight Enclosure, Air Filled

Enclosures can be designed that are only relatively gas-tight, and normal air atmospheres can be maintained in such enclosures to prevent the cost of continuous inerting. If an alkali-metal leak occurs in such an enclosure, the fire may be self-extinguished by oxygen depletion within the enclosure, or it may be smothered by flooding with an inert gas such as argon, helium, or nitrogen.

The degree of oxygen depletion necessary to extinguish the fire will depend upon the type of leak. During a sodium spray leak, the oxygen concentration in the enclosure would have to be reduced below 4 vol % to prevent burning, and formation of airborne oxide would continue for oxygen concentrations down to 0.5 vol % and possibly to 0.1 vol %. If release of dispersed sodium ceased and the sodium was burning in a pool, oxygen depletion to about 10 vol % might stop "burning" and start a slow cooldown of the pool. In either case, the reignition characteristics of the molten metal

require that the low oxygen concentrations be maintained for a significant period of time to permit cooling of the metal (and stopping the spray).

Unfortunately, the design criteria for the construction of a "relatively" tight enclosure must be based upon engineering judgment with a minimum of sound technological input. Obviously, we are considering the case in which extreme leak tightness of the enclosure is not required because, if it were completely tight, an inert atmosphere would be justified. During the early stages of a sodium fire in the enclosure, the sodium oxide aerosol will deposit fairly uniformly over the inside surfaces of the enclosure and will often seal the seams of the enclosure and prevent or reduce the ingress of oxygen necessary to support combustion of the sodium. One advantage of this type of enclosure is retention of most of the generated alkali-metal oxides within the enclosure. Because smoke damage to surrounding equipment is often extensive in unenclosed fires, this advantage is significant.

Although this type of enclosure closely resembles the inert enclosure, it has one significant difference: With an initial air atmosphere, releases of high-temperature alkali metal will always result in a fire. For this reason, the enclosure must be sufficiently substantial to withstand the heat from the fire and, with pressure relief mechanisms, the pressure surge that will occur.

Sodium fire suppression by oxygen depletion offers an opportunity for engineering research which might prove of substantial value to future LMFBR facilities; existing data are not sufficient for a reliable evaluation of this method of sodium fire control.

3. Air-filled Semienclosure That Can Be Converted to Complete Enclosure

Due to ventilation (heat removal) requirement or the requirement for frequent access, some facilities may not permit complete enclosure. Often, such a semienclosure can be converted to a complete enclosure by automatic (fire damper) or operator action. Because of the marked similarity to the relatively gas-tight enclosure, special comment is not warranted.

4. Semienclosures That Confine Spilled Sodium or NaK to a Specific Area

One of the more prevalent types of situation in ANL experimental work involves semienclosures or splash shields which direct leaking alkali metal into a pan or tray beneath the experimental equipment. In the event of a metal fire, this situation will result in the release of some alkali-metal oxides into the room, but should pose no significant problems in extinguishment since the fire should be easy and safe to approach to permit the application of an inert dry powder extinguishant. The complexity of extinguishment

and the amount of powder required will vary depending upon the specific alkali metal the depth of the spilled-metal pool, the physical arrangement of the equipment, and the use or nonuse of a perforated plate within the tray or pan.

Extinguishment of an alkali-metal fire essentially consists of preventing oxygen from diffusing to the molten or gaseous metal and maintaining this state until the metal has cooled below the ignition temperature. At ANL, current firefighting practices for sodium and NaK fires involve the use of dry silica sand or MET-L-X (fine, treated NaCl) to provide the oxygen barrier. Dry soda ash is also referred to in the literature as an extinguishant, but care must be exercised to ensure that it is moisture free. The value of any of these extinguishants is apparently enhanced if the molten metal is confined in a pan and if the pan is provided with a perforated plate located at an intermediate depth in the pan. In some cases, it is reported that the perforated plate alone acts as an oxygen barrier and extinguishes the metal fire; additional studies on the use of perforated plates are, however, warranted. NaK fires are particularly hard to extinguish, and the manufacturer of MET-L-X recommends that a perforated plate always be used in NaK drip pans and that the plate be positioned so that if all the NaK was released it would be within 1/2 in, of the surface of the molten metal. In the design of collections pans (particularly for potentially large sodium spills), consideration must be given to thermal effects on the supporting floor. For example, a large pressure of steam could be generated under the pan due to trapped moisture or thermal decomposition of concrete. Therefore, the space between the floor and the metal liner may need to be vented to prevent excessive pressures from steam.

The ideal powder extinguishant for sodium or NaK fires would have a particle density less than the bulk density of the molten metal so that all the extinguishant would remain at the top of the molten metal. Neither silica sand, soda ash, nor MET-L-X have this advantage. Each has a theoretical particle density at least twice that of molten sodium or NaK, and therefore each must be gently dusted onto the surface of the molten metal to take advantage of surface effects (perhaps nonwetting, or possibly due to a sodium oxide scum or a reaction product between the sodium oxide and the extinguishant). When gently dusted, both the sand and the MET-L-Xin contact with burning sodium, and less so with NaK, form a crust which permits the gradual buildup of a sufficiently thick layer of extinguishant to stop the fire, (See p. 61 of Ref. 10; this reference is summarized in Section 3 of Appendix C.) In contrast, rapid application of these powder extinguishants results in the particles sinking into the molten metal and becoming ineffective as a blanketing agent.

The above considerations have a serious effect upon the quantity of extinguishant needed to put out an alkali-metal fire. In tests using MET-L-X applied to burning sodium from a conventional pressurized cylinder and with a shovel, the MSA Research Corporation found that the fires were

extinguished with 0.2-0.8 lb of extinguishant per pound of sodium. (An abstract of Ref. 11 appears in Section 4 of Appendix C.) Shovel application resulted in the lower extinguishant-to-sodium ratios. Extinguishing tests by other experimenters, however, indicate that higher MET-L-X-to-sodium ratios are required. Atomics International found¹⁰ that the required weight ratio varied from 0.8 to 4.2, the larger ratios being required when the MET-L-X was applied before the burning sodium reached equilibrium temperature (~1200°F). The Ansul Co. (manufacturers of Met-L-X) and the Underwriters' Laboratories are even more conservative. In discussing agents for use on combustible metals with specific reference to MET-L-X, the Underwriters' Laboratories state:

"Molten sodium and potassium which are confined to a definite area and are in depths greater than 1/2 in. require approximately 6 lbs of agent per square foot of area or per pound of fuel. Molten sodium-potassium alloy in depths less than 1/2 in. requires approximately 15 lbs of agent per pound of fuel, or 10 lbs of agent per square foot of area.

"Molten potassium and sodium-potassium alloy fires in depth require the use of a grate above or not more than 1/2 in. below the surface of the burning metal. The grate is comprised of a steel plate having about 35 percent of the area opened by 3/8-in. holes spaced 9/16 in. on center."

The extinguishant-to-fuel weight ratio is not as thoroughly documented for sand as it is for MET-L-X. This is probably partially because of the wide variety of sands used and the variations in their degree of dryness. Atomics International found¹⁰ that when using "Crystal White No. 30" sand, the extinguishant-to-fuel weight ratio (sand/sodium) ranged from 2.1 for the dry sand to 8.4 for the nondried sand. When using "Foundry" sand, they found the ratio for the dried sand varied from 1.8 to 4.8.

The choice between MET-L-X and silica sand for fighting sodium or NaK fires is generally based on economics, convenience, and whether remote dispersal is required. For small fires, MET-L-X is probably preferable because of the convenience of using small portable extinguishers containing material of guaranteed dryness. For larger fires, where direct approach is possible, sand is probably preferable because it is cheap and therefore can be stored in quantity. For large fires, where direct approach is impractical, MET-L-X must be used because remote dispersal systems are not available for sand. Where chloride stress corrosion is a worry, calcium carbonate may be preferred. ¹³

Sodium and NaK fires restricted to definite regions by semienclosures and drip pans should not be difficult to extinguish unless the area or the quantity of metal spilled becomes very large. Sufficient dry powder extinguishant should be kept in the immediate vicinity of the sodium or NaK equipment. Because the ratio of extinguishant to molten metal may be quite high, a combination of extinguishants may have to be provided. MET-L-X could be used in sufficient quantity to extinguish a fire in which only a portion of the available metal spills, and silica sand could be used to extinguish a fire in which all the available metal spills.

5. Sodium or NaK Spills in Open Areas

Some sodium facilities have been built in open areas so that the leaking metal has no confinement either in the form of splash shields or drip pans. Such installations offer more problems in firefighting than those previously discussed. The floor surface is often steel, but in some cases it is concrete, or even earth. With concrete or earth floors, firefighting is particularly difficult because the dripping or running molten metal frequently reacts violently with the floor, thus endangering the firemen and widely scattering the burning metal.

The main effort in extinguishing a sodium or NaK pool fire in an open area consists of restricting its spread. Because the rate of liquid-metal oxidation in a pool is directly proportional to the surface area, limiting the surface area can minimize both the direct fire damage and the quantity of sodium oxide smoke formed. Experience has shown that even rather large volumes of sodium can be contained by perimeter diking using dry sand, lead bricks, lengths of pipe, or practically anything else that can make a firm contact with the floor over an appropriate length. Once a sodium spill is diked, sand or MET-L-X can be used to extinguish the fire.

6. Sodium or NaK Drippage or Sprays from Elevated Leaks, No Enclosure

Because sodium facilities are constructed, in general, above floor levels, leaks would, of necessity, be in elevated locations with the sodium dripping or spraying from the leak site, depending upon the system pressure and configuration. The spray is usually burning. To control a flowing or dripping fire, some method must be available to drain the system, to isolate the section that is leaking, or to close off the leak with a heat-resistant enclosure which can be put into place under adverse conditions. Such an enclosure, usually made of metal, would have to be custom-made to fit over potential sources of leaks such as expansion bellows, valve bonnets, and test sections. In the absence of these methods of control, the only alternative is to build up a dry powder hill to cover and possibly plug the leak. MET-L-X will frequently adhere to molten metal on vertical surfaces and extinguish the fire on such surfaces if the molten metal is relatively stagnant.

Spray fires cannot be put out unless the oxygen in the gas phase can be reduced in the spray region to low levels and maintained at these levels for the duration of the spray. To achieve this, the facility design

should tend to isolate and minimize the volume of the probable spray region, minimize the oxygen in (or the ingress of oxygen into) the region, and minimize the time that the spray can exist. Minimizing the volume of the probable spray region can be simple for small pieces of apparatus. These can be completely enclosed, with the enclosure envelope filled with nonhygroscopic packing materials such as vermiculite. Such installations also tend to extinguish the fire by limiting the access of oxygen. Particular attention should be paid to flanges and other remakable joints. Design provisions to limit the duration of a spray should include dump tanks and associated dump valves and means for depressurizing the system either by venting pressurizing gases or by deenergizing circulating pumps. (Dump tanks are regarded as a very important method for controlling or preventing a sodium fire.) In essence, a spray fire in air cannot be fought--it must be prevented, or the spray must be stopped.

7. Combined Sodium and Ordinary Combustible Fires

Burning sodium or NaK has a small flame height, because of the limited vapor-phase burning of the metal. However, if conventional combustibles are ignited in the region of the fire, the fire can readily spread. This is a very serious problem and is compounded by the fact that the extinguishants normally used on conventional combustibles are dangerous to use near alkali-metal fires, and such fires will probably result in serious risks for the firefighters and in extensive property damage. The extinguishing agents normally used on sodium fires (sand or salt) are usually completely inadequate for extinguishing fires of flammable liquids and ordinary combustibles.

The ANL Fire Department recommends the use of dry silica sand (or MET-L-X) in conjunction with a multipurpose dry chemical agent (mono- or diammonium phosphate) for combined sodium and ordinary combustible (or flammable) fires.

Combustible materials (also <u>any</u> extraneous materials) in alkalimetal areas should be limited to an absolute minimum.

This problem was studied in some preliminary experiments with sodium and tetralin fires at Atomics International. ¹⁴ In these experiments, it was concluded that the best method for handling a combination fire is the sequential use of a dry, inert powder to suppress the sodium fire, followed by carbon dioxide. Other workers have recommended the use of carbon dioxide first, followed by a powder extinguishant for the sodium fire. This combination of firefighting agents would probably be effective only for relatively small, organic-sodium fires.

8. Sodium or NaK Fires in Regions with High Radiation Backgrounds

In a few ANL facilities, all at Idaho, sodium or NaK systems are operated in regions in which the gamma-radiation background prohibits

direct access. Usually the gamma source is the alkali metal itself. Fire-fighting in this case is exceedingly difficult. Normally, the facility is provided with a fixed, remotely actuated MET-L-X system. The efficiency, and even the adequacy, of this fixed system, however, is severely limited by the inability to determine the extent of metal leakage and if the leakage has terminated. Such systems should be provided with means to determine the extent and duration of leakage. If practical, the systems should also be provided with inert-atmosphere enclosures, or means should be provided to apply such an atmosphere if a fire develops.

B. Effects of Alkali-metal Oxide

In addition to the extinguishment problems discussed under the above eight situations, the serious effects of the alkali-metal oxide which is produced in the fire must also be considered. This oxide aerosol will severely reduce visibility in the region of the fire and will, therefore, severely hamper firefighting activities (see Appendix C). If the smoke is allowed to spread, it can seriously damage equipment in adjacent regions and present a health hazard to unprotected personnel.

Self-contained air-breathing equipment is standard emergency equipment in sodium facilities at ANL and is used with full protective clothing to protect firefighting personnel from the smoke and from possible oxygen depletion of the atmosphere in the immediate vicinity of the fire. However, the problem of seeing through the dense oxide smoke has not been resolved and seems worthy of research effort. (The ANL Fire Department is conducting tests with an infrared detector.)

Smoke within a building containing a sodium fire can be reduced by using proper ventilation equipment. Such reduction improves firefighting capability and minimizes caustic damage to equipment within the building. To prevent damage to personnel and equipment outside the building, the exhausted air should be scrubbed to remove the aerosol. Provision of an air scrubber should be considered for all buildings using significant quantities of sodium. This can be achieved by a venturi or cyclone scrubber, a water-film scrubber, or an electrostatic precipitator. Filters can also be used; however, they must be large enough to prevent "plugging" by the sodium oxide.

After each sodium or NaK fire, two stages of cleanup will be required. The mass of metal, oxide, and extinguishant will have to be safely disposed of. This mass will doubtlessly contain significant quantities of unreacted metal, which will reignite if carelessly handled. In addition, alkali metals can form peroxides and higher oxides. The lower oxide (M_2O) is formed if the oxide is in equilibrium with excess alkali metal; in the absence of excess metal at equilibrium, the higher oxides can be formed (depending upon temperature and partial pressure of oxygen). These higher oxides are strong

oxidizing agents and can react explosively with alkali metals and organic materials. (See Section 3 of Appendix E.) Thus the residue from an alkalimetal fire (particularly potassium, rubidium, and cesium) should not be stored in contact with organic materials and the residue should be transported (as soon as practical) to a site where it can be safely reacted to completion and then disposed of.

The second stage of cleanup will consist of cleaning the surrounding area and equipment. The damage to exposed wire, general laboratory equipment, and painted surfaces can be extensive. Unpainted surfaces are sometimes used to avoid the need to repaint areas susceptible to sodium fires. The smoke damage to some precision equipment could be extensive enough to make salvage questionable. Such equipment, therefore, should be designed to minimize smoke damage. In one such proposed application at ANL, expensive data-acquisition equipment is located in a separately ventilated "clean room" adjacent to the serviced sodium loop.

In summary, sodium and NaK firefighting is complicated by the high reactivity of the metal, problems in visibility, configurations of equipment, heat levels, and limitations of extinguishing agents. These complications require great emphasis on better design criteria leading to fire prevention and on fire-control methods in the design stage of each facility.

V. GENERAL CONCLUSIONS AND RECOMMENDATIONS

A. Effectiveness of Sodium Firefighting Methods

Studies of the literature have not disclosed fully effective methods for fighting sodium fires, particularly fires associated with overhead leaks, deep pools of sodium, or radioactive sodium. Several extinguishing agents have been tested which show promise for very specific cases, such as fires involving both sodium and tetralin, but each agent has drawbacks. Only MET-L-X (treated NaCl), high-quality sand, calcium carbonate, and soda ash of guaranteed dryness appear generally applicable for sodium and NaK fires of the type anticipated with conventional sodium systems. The difficulty in guaranteeing the dryness of soda ash generally eliminates this material from serious consideration. In a few cases with favorable geometry, fires once started in an air atmosphere may be extinguished by the application of inert gas, but the required degree of inertness (~0.5 at. % oxygen), the duration of application to prevent reignition, and the uncertain effects of thermal-convection currents reduce the applicability of this method of extinguishment.

Because of these limits upon firefighting capabilities, great emphasis must be placed upon means to minimize the possibility of a sodium or NaK fire, to prevent its spread, to limit its duration, and to minimize the potential damage to the surroundings. Prevention of a fire is the ideal approach,

and this can be accomplished by total enclosure and continuous maintenance of an inert atmosphere. The cost of such an approach is significant, but the potential benefits warrant this expenditure when the probability of a fire is high or the consequences would be very serious. Where practical, dump tanks should be used to reduce the magnitude of a potential fire.

Efforts to minimize the probability of a fire and to limit its consequences require responsible action by the designer and installer of experimental equipment, by the operator, and by departmental management in assigning the experimental space. These individuals should be guided by concise, readily available laboratory policies and procedures and by safety indoctrination and training programs. The supervisor must ascertain that each operator is fully aware of emergency procedures to be followed in case of a fire.

Because sodium and NaK work is so greatly diversified, it is difficult to establish Laboratory policies and procedures that are both pertinent and nonregressive. We suggest the following:

- 1. Each new installation involving more than 10 lb of alkali metal and each radical change in scope or location of existing installations shall be brought to the attention of the Fire Protection Department and other Emergency Groups at an early stage. Notification shall be in writing, using a form generally similar to the Sodium Facility Survey sheet (in Appendix A).
- 2. Each new installation or operation involving more than 10 lb of molten or 100 lb of solid sodium shall be subjected to departmental review by personnel not intimately associated with the design, installation, or operation.
- 3. An updated concise statement of procedures and responsibilities for disposing of contaminated and noncontaminated waste alkali metal shall be maintained by the laboratory. Also include:
- a. F. A. Anderson, A Primer for the Safe Use of Liquid Alkali Metals, ORNL-TM-174 (see Section 1 of Appendix E),
- b. Manufacturing Chemists' Association, Inc. Chemical Safety Data Sheet SD-47 or NSC Data Sheet 231, and special booklets and procedures specific to the Laboratory operations.
- $\begin{array}{c} B. \quad \underline{\text{Need for Research and Development on Extinguishing Agents and on}} \\ \overline{\text{Extinguishment of Large Sodium Fires}} \end{array}$

Available extinguishing agents for sodium and NaK fires are far from ideal, despite appreciable investigation. We believe that extinguishment of very large (thousands of gallons) molten-sodium fires with conventional

extinguishing agents should be investigated by an agency with experience with large sodium fires. For these potentially very large sodium fires, the only suitable approach may be one of fire prevention by use of a "fail-safe" dump-tank system or by providing an inert-atmosphere enclosure for the sodium system. For some applications and with a suitably designed enclosure, oxygen "starvation" of the potential fire may be a satisfactory solution.

We believe that additional studies of all types of sodium fires are warranted; information from such studies could be very valuable to future stages of the LMFBR program. We recommend that new sodium-fire extinguishing agents be investigated. Such agents should include the following:

- 1. Free-flowing powders, which can be easily distributed a significant distance by pipe or hose. One product on the market (treated KCl) is reputed to be such an agent. [If KCl can be prepared in this manner, one would expect the same for NaCl. However, the hose discharge distance for MET-L-X (NaCl) is relatively small.
- 2. Low-density powders that would float on molten sodium. Fine vermiculite,* dried and specially treated to prevent sorption of water, might be such an agent.
- 3. Flexible blanket materials which could be wrapped around a slow, elevated sodium-leak. Woven stainless steel* might be such a material.

C. Visibility, a Major Handicap

Visibility is a major problem in fighting a sodium fire. There is a great need for developing a device that would provide a visual method for directing sodium firefighting activities, and the Committee recommends R&D type effort on this problem. An "infrared scope" might be a useful device; however, the effectiveness of this type of device may be significantly reduced by dense sodium oxide smoke.

D. Use of Drip Pans with Perforated Plates

Almost all studies reported in the literature** of NaK or sodiumhazard control recommend the use of drip pans beneath molten-metal-filled apparatus to prevent violent reaction of dripping metal with concrete or similar floors and to restrict the area of the resulting pool fire. Ideally, the pan should be beneath all portions of the apparatus, but where this is impractical, pans should at least be located beneath those portions most apt to fail. Many of the studies further recommend that the drip pans

^{*}Use of this material for sodium firefighting has been discussed in a few reports. (See, in particular, Ref. 11.)

^{**}These recommendations, however, appear to be based solely on experimental studies by the Ansul Company.

include a grate (perforated plate with 30-35% open area as staggered holes) which will greatly simplify the problem of fire extinguishment. The Ansul Company (manufacturer of MET-L-X) states that such a grate is essential in fighting NaK pool fires.

In the design of the collection pans, possible thermal effects upon the supporting floor must be considered (for example, thermal decomposition of concrete).

E. Sodium-fire Detection Problem

Many sodium and NaK experiments must be maintained at elevated temperatures during unattended off-shift periods. During these periods, the normal protective device used to alert emergency crews is an ionization smoke detector. Experience with the ionization type of detector in the past has been poor. These detectors are relatively insensitive to Na₂O fumes and very sensitive to fumes from some conventional fires. This situation has caused apathy towards their use and has frequently resulted in their being installed in poor locations. To alleviate this situation, the Committee makes the following recommendations:

- 1. The use of sodium smoke detectors is recommended, but the choice of the appropriate detector should be based upon the detectors' sensitivity, reliability, and ease of maintenance. The detector should be located with great care, particularly in regard to airflow patterns.
- 2. Where experiments with liquid metals have a high probability of leakage due to high temperatures or other borderline conditions, or the consequences of delay in fire detection could be very serious, the smoke detector should be supplemented with an appropriate leak detector.

F. Design of Total Enclosures

There is an increasing tendency to use enclosures (with either a stagnant air of inert-gas atmosphere) because the present level of technological investigation requires more strenuous demands upon the loop materials, enhancing the probability of leakage. Such enclosures, however, might offer false security and even increase the hazards of a leak, if the enclosures are inadequately designed. The wall panels should be made of materials which are strong, and ductile, will withstand high temperatures, and which will not readily react with molten sodium. The enclosure should be provided with a pressure-relief mechanism, and the design of the wall panels and their fastenings coordinated with the pressure-relief mechanism. Gracie and Droher (Ref. 10, pp. 24-37) point out that spray burning of sodium can cause the pressure in enclosures to go at least as high as 85 psig if unrelieved. (Also see Ref. 16.) Also, if continuous inerting is used as protection, the extent of inerting must be continuously ascertained. The Committee recommends that:

- Walls of total enclosures be made of materials such as steel, which will not readily react with molten sodium or rapidly fail due to pressurization or heat from a fire.
- 2. Pressure relief be provided for the enclosures.
- Inert-atmosphere enclosures be provided with means to either periodically or continuously monitor and log the oxygen concentration in the enclosure, the choice dependent upon the degree of risk.
- 4. Sodium leak detection methods be provided.

G. The Need for Additional Research and Development on Materials

The Committee was particularly impressed by the following:

- 1. There was frequent reference in the literature to failures of bellows-sealed valves, but little information was found on why these valves failed (see Appendix D).
- 2. In Section II.A of this report, the extensive, exterior corrosion of flanges, vessels, etc., resulting from relatively small sodium leaks was discussed. Very little information could be found in the literature as to why and under what conditions this extensive corrosion occurs.
- 3. There appears to be a need for an enhanced effort on understanding failure mechanisms for sodium systems.
- 4. The anticipated operating temperature (~1050°F) of the LMFBR plants is significantly higher than the temperature at which most of the sodium operating experience exists (700-800°F).

APPENDIX A

Sodium Facilities Survey

ANL AD HOC GROUP ON SODIUM FIRES SODIUM FACILITIES SURVEY

Location: Bldg. 308, Central high bay, Bldg. Areas V and VI.

Title: Core Component Test Loop (CCTL).

Experimenter: F. A. Smith (ETD).

Type Work: Isothermal hydraulic flow test of fuel subassemblies and re-

lated instruments.

Capacity: 900 gal.

Temperature: 1200°F (design); to be operated to 1150°F.

Pressure: 150 psig--design.

Flow: 800 gpm.

Construction: Largest size of piping -- 5 in. suction, 4 in. discharge; all

304 stainless steel; all welded with exception of flanged

fittings above sodium level.

Containment: Entire loc; is installed within a 20 ft deep, steel-lined, pit of

dimensions 20×25 ft; openings at the top of the pit can readily be closed by the equipment operators. The dump tank is enclosed with sheet steel. The top steel deck is insulated

(3-hr rating; UL Test No. R-3749-3).

Drainage Capability: A 920 gal capacity dump tank can accept the loop

contents through a 2 in. drain line.

Cover Gas: Argon.

Fire Protection: Portable and wheeled dry powder (MET-L-X) extinguishers are available for small leaks. A larger leak would be con-

tained by closure of pit openings and introductions of argon gas into the bottom of the pit; a manually operated manifold system, located on the south wall of the high bay area, discharges through copper tubing into the pit.

Fire Detection: Ionization type smoke detectors at ceiling in pit and high bay area; an additional detector is to be installed in the pit.

A survey is being made to update the detection system.

Leak Detection: Only visual observations by operators; prior to future operation, resistance wire type of leak detection is to be

provided at the bonnets of all the drain line valves.

Operation: 24 hr basis, under supervision, when operating; well planned

shutdown procedures have proven effective when leakage oc-

curred on April 17, 1969.

Future Scale: Same.

Reference: "Sodium Test Facility Questionnaire" is attached. For addi-

tional information see "FARET Fuel Assembly Flow Test Facility"--paper presented at A.N.S. meeting June 1965.

Potential Hazard: A catastrophic failure resulting in the loop contents being spilled into the bottom of the pit might seriously challenge the capability of the protective features of the facility; the most serious accident, however, that might seriously be postulated is a sizable leak where the sodium was well dispersed and rapidly oxidized. The heat generated could conceivably destroy the integrity of the metal covering of the pit; control of the fire would then be most difficult and considerable quantities of smoke would be released into the building. Only a limited quantity of argon gas (4 cylinders) is held in reserve for use in the pit if the "containment and self limiting combustion principle" fails; additional cylinders are located within the building but not as readily available.

APPENDIX B

Sodium Leak and Fire Detection and MET-L-X Systems

1. Sodium Leakage Detection: State-of-the-Art Study, LMEC-Memo-69-35

Sodium Leakage Detection State-Of-The-Art Study

by K. A. Davis



Liquid Metal Engineering Center



Operated for the U.S. Atomic Energy Commission by Atomics International

Contract: AT(04-3)-700

Issued: February 16, 1970

CONTENTS

		Pag
	Abstract	5
I.	Introduction	7
II.	General Discussion	9
	A. Scope of Study	9
	B. Sources of Information	9
	C. Sodium Leakage	10
	l. Methods of Leakage Detection	14
	2. Sodium Behavior at a Leak	15
III.	Instruments for Detection of Sodium Leakage	19
	A. Leak Detection by Sensing Liquid Sodium	19
	l. Electrical Circuit Methods	19
	B. Leak Detection by Sensing Sodium Vapor	27
	l. Analytical Chemistry Methods	29
	2. Light-Emission Methods	30
	3. Light-Absorption Methods	31
	4. Leak Detection by Radioactivity Sensors	31
	C. Leak Detection by Forming and Sensing a Reaction Product	33
	1. Smoke Detection	33
	2. Specific Chemical Reagents	34
	3. Sodium-Sensitive Materials	35
	D. Sodium Leakage Into a Liquid	35
	l. Sodium Leakage Into Sodium	36
	2. Sodium Leakage Into Water	36
	References	37
	TABLE	
1.	Operating Systems I eakage Incidents	

FIGURES

		Page
1.	Leak Detector Probes Enclosed in a Jacket	23
2.	Schematic Diagram of an Optical Sodium Vapor	32

ABSTRACT

Leakage of sodium from its container and methods of detecting such leaks are reviewed (leakage of water into sodium is not included in the discussion). Emphasis is placed on the various types of instruments which may be applicable; the operating principle, performance factors, and status of each type are presented. The discussion includes proposed leak-detection methods as well as those which have been evaluated experimentally.

I. INTRODUCTION

The need for sodium leak-detection methods varies over a wide range from little more than personal observation and alertness of the operators in small systems, to fast-response, high-reliability, continuous surveillance instrumentation for very large systems.

Many techniques have been studied; a few have been evaluated in 'bench tests,' still fewer have been used in operating systems. Performance evaluation data on the various methods are incomplete and generally are inconclusive because of the limited means of evaluation. There is general agreement that while some types have performed well in specific cases, the range of conditions for satisfactory operation is very limited and no single contemporary instrument. is regarded as satisfactory for general usage. A combination of instruments often is used to meet the leak-detection objectives for a complex system.

The main problem with all contempory instruments is in getting the leaking sodium to the sensor. Reliably actuating the sensor is somewhat less a problem.

Methods which depend on sodium reaction to create a readily detected reaction product, or to cause a readily detected property change, appear more amenable to successful development than the contemporary instrument.

In sodium-to-liquid leakage, as in the case of heat exchangers, the number of techniques possible is relatively small.

II. GENERAL DISCUSSION

A. SCOPE OF STUDY

This report presents a review of various methods used to detect sodium leakage; particular emphasis is given to instrumentation techniques. The study was concentrated solely on the leakage of sodium from its container. Typical examples are: sodium leaks to the surrounding atmosphere from pipes, vessels, and other components; or leaks to another fluid in heat exchangers. Leakage of an external fluid into the sodium container was not considered. This excludes a large segment of sodium leak-detection technology commonly involved in sodium-heated steam generators in which a leak ordinarily is from the water side into the sodium.

The phenomena which are used, or appear to be applicable, in leak detection instrumentation are reviewed. The feasibility and extent of use, and the apparent success or acceptance of the various techniques are discussed.

B. SOURCES OF INFORMATION

This study was conducted by reviewing the pertinent technical literature, followed by discussions with persons engaged in sodium technology at several of the various facilities which have operating sodium loops.

The technical literature contains relatively few details concerning sodium leakage and methods of detection. Several reports of the early 1950's indicate concern about techniques of leak detection. For example, a study of sodium leak-detection methods was conducted by Mine Safety Appliances Company (MSA) and was reported in a series of reports beginning in 1952. (1-5) For a number of years thereafter, relatively few reports of a substantial nature were published. Many of these publications were internal documents or were otherwise of limited distribution. They generally contained descriptions of proposed systems and sometimes presented preliminary data on bench tests. Relatively little data have been published on the performance of leak-detection methods in operating systems. Generally, leakage is a subordinate topic in progress reports on system or component operation; leaks are discussed only in sufficient detail to account for a slowdown in the operation. The method of leak detection seldom is mentioned; and even when mentioned there is little evaluation or information for evaluation of the method.

The lack of published data is understandable since there are so many negative aspects of sodium leak-detection technology. Unlike the operation and evaluation of other instruments, the condition which yields leak detection performance evaluation data is undesirable to say the least. Moreover the conditions existing during a leak are not conducive to good observations or the acquisition of useful engineering data.

A literature search of leakage incidents in operating systems yielded the data presented in Table 1. The purpose of the search was to determine the nature of the detection method used. As shown, very few reports indicated this.

The information gained by conference filled in a few of the gaps but most of this information simply confirmed the picture developed by report review and analysis.

C. SODIUM LEAKAGE

Sodium leakage, though always undesirable, may be tolerated in some cases; in other situations immediate remedial action is required to prevent damage. The significance of a sodium leak depends on its size, character, and location, and the system function and vulnerability to leak damage.

A range of views on methods of dealing with sodium leakage detection is prevalent. At one extreme is the effort to provide a method, or methods, which will assure detection of any leak. While this is an ideal objective, it is not conveniently achieved with any contemporary techniques. The wide range of possible leak situations, especially in large systems, requires a number of specialized surveillance methods. An attempt to achieve complete and reliable surveillance, with contemporary instruments, leads to an unwieldy and expensive leak-detection system. At the other extreme, is the omission of any formal leak-detector system on the basis of either: an acceptable risk with no leak information, or reliance on evidence provided by other instruments or operational conditions. The typical approach is a compromise between these two extremes: an effort to map the regions in terms of probability of leaks and assign surveillance methods; or to proportion the effort to the various regions according to the needs of the region. This approach requires assumptions regarding: (1) component susceptibility to leakage; and (2) the leakage behavior and effects.

Component	Leak Location	Method of Detection	Conditions	Ref.	Page No.
Valve, Bellows Sealed	Bellows	-	N	6	10
Flange	Flange	-	A	6	26
Valve, Bellows Sealed	Bellows	-	N	6	28
Valve, Bellows Sealed	Bellows	-	N	6	28
Valve, Bellows Sealed	Bellows	-	N	7	15
Valve, Bellows Sealed	Bellows	-	N	7	15
Pipe, 1/2 in.	Pipe	-	N	6	10
Valve, Bellows Sealed	Bellows	-	· N	8	9
Valve, Bellows Sealed	Bellows	-	N	8	9
Valve, Bellows Sealed	Bellows	_	N	9	11
Valve, Bellows Sealed	Bellows	Swift eignät	N	10	4
Flange	Flange	ebeniga za	A	11	11
Flange	Flange	1 1 1 1 1 1 1	A	11	11
Valve, Bellows Sealed	Bellows		A	12	7
Intermediate Heat Exchanger	Tube Sheet Weld	(1)	N	13	23
Piping	Pipe Joint	-	N	14	63
Thermocouple Well	Well	-	N	15	233
Tubing, Heater	Tube	(2)	N	16	123
Expansion Tank	Tank	-	A	17	109
Piping	Pipe	-	N	18	196
Flange Joint	Flange Joint	-	N	18	211
Piping	Pipe	_	N	18	229
Piping	Mechanical Joint Seal	_	N	19	501
Sodium Cooler	Cooler	_	N	20	1083
Valve, Bellows Sealed	Bellows	-	N	20	1152
Sample Holder	Holder	-	N	20	1165
Linear Induction Pump	Pump Duct	(3)	N	20	1255

TABLE 1

OPERATING SYSTEMS LEAKAGE INCIDENTS (Sheet 2 of 2)

Component	Leak Location	Method of Detection	Conditions	Ref.	Page No.
Test Apparatus	Bellows	2490 22234	N	20	1284
Piping	Pipe	1	(7)	20	1286
Thermocouple Well	Well	(4)	N	20	1288
Piping	Nozzle	-	N	20	1317
Valve	Valve Packing	. a. 16237 a.	N	20	1360
Valve	Bellows	the long fam	N	20	1366
Valve	Bellows	over-loye m	N	20	1366
Valve	Bellows	Tarin Magazine	N	20	1366
Sodium Freeze Trap	Thermocouple Weld	(5)	N	21	2
Pipe Joint	Weld	(6)	N	22	840

Notes:

- N Normal (presumed)
- A Abnormal
- Not stated in the reference report
- (1) Leakage was not detected while the component was in operation. The evidence of leakage was discovered during cleaning after operation.
- (2)Smoke observed.
- (3) The leak detector (kind unspecified) in the case of the main secondary linear induction pump sounded an alarm. Visual inspection confirmed that the pump duct had developed a leak.
- (4) Certain core elements temperatures were observed to be erratic. The reactor was shut down and the subsequent examination revealed sodium leakage into a thermocouple well causing a shorting of the thermocouples.
- (5) Report, Ref. 21 did not indicate the method of detection. An oral inquiry revealed that the leak was discovered by operating personnel hearing a sputtering sound and seeing flashes of light. Investigation showed this to be leaking sodium.
- (6) Electrical contact.
- (7) The failure occured in a straight run of pipe and may have been the result of trace heater arcing to the pipe, but this could not be definitely determined.

The susceptibility of a component to leakage is a function of: (1) its material properties and fabrication method, especially the associated material failure mechanisms; (2) the effect of operating environmental conditions; and (3) the effect of operation (or maloperation). The susceptibility is of significance in selecting a leak detection method since the factors involved determine the nature of leak development; the main concern here being the speed at which the leak progresses. For example, if the leak is a small hole in an otherwise unimpaired wall, and the sodium flows away from the surface without prolonged contact and flows into a drip pan or other harmless region, it is improbable that substantial damage or a catastrophic event such as a major rupture would occur before corrective action can be taken. However, the same leak, if covered by typical thermal insulation so that the leaking sodium cannot leave the surface, will result in prolonged contact of the sodium reaction products with the wall surface, causing corrosive action which results in a thinning of the wall over a substantial area. Then a pressure or thermal transient could cause bursting and substantial sodium-caused damage.

Thus some leak-causing factors are of a nature that the time from the initial break to an extensive rupture is very short so that severe damage is almost certain before corrective action can be taken.

An analysis of the component susceptibility to leakage should be made prior to design or selection of a leak-detection system. A detailed treatment of the susceptibility factors is beyond the scope of this report. However, a few general remarks are appropriate.

The design and fabrication quality requirements usually imposed on sodium containment structures, and the leak testing and repair prior to operation with sodium minimizes the possibility of leaks. When leaks occur, they often occur at points of high stress concentration and at points of impaired structural properties such as at inclusions or regions susceptible to fatigue failure. Generally, the regions of potential leakage are considered to be around welds or in thin sections subjected to cyclic stresses such as at bellows or diaphragms or in regions subjected to severe thermal shock.

A study is in progress to investigate sodium leakage through stainless steel into air. (23) The research has four goals: (1) to provide an understanding of the

mechanism of leak path plugging and reopening in sodium-stainless steel systems; (2) to determine realistic standards for leak tightness and establish reliable techniques for finding the leaks; (3) to correlate time to sodium leakage with the initial leak path as measured on a helium mass spectrometer; and (4) to determine oxygen intake into sodium systems through leaks.

1. Methods of Leakage Detection

Often leak detection is accomplished without the use of any apparatus specifically designed or installed for leak detection. Instruments and operations established primarily for other functions can provide leakage indication hence the leak detection function is incidental. This approach is common and often is satisfactory. In many cases, especially in development or test systems and in the secondary coolant circuit of reactor systems, visual observation provides an excellent means of detection. In the case of a large leak, the issuance of the liquid metal is readily apparent. A small leak may be noticeable if the sodium reaction with the atmosphere produces a noticeable deposit on nearby surfaces. Depending upon the circumstances, the reaction may result in smoke or fire. When the leaking component is in a small enclosure such as a vacuum vessel, a sodium vapor condensation or smoke deposit is evident on the view ports. Where components are located in an area which precludes close personal observation, television type surveillance can be used, in some cases, depending upon the nature of the system. Personal observation of the televised image is necessary in simple surveillance systems but circuits responding to changes only can be used to provide an alarm signal, alleviating careful personal observation.

Another common method involves the observation of unexpected changes in process quantities such as pressure, flow rate, or volume (level). Sodium leaking to the outside certainly results in a decreased quantity within the containment vessel. The resolution of the usual instruments for measuring the quantity of sodium in the vessel is too coarse to indicate small leaks in a large system within a reasonable period of time. However, in some cases, generally in relatively small systems, this method is adequate. This is done in space systems by monitoring the magnitude of the expansion in the expansion compensator.

The leak-detection techniques described briefly in the preceding paragraphs did not involve instruments designed or used specifically for sodium leakage detection.

Many small sodium systems are operated without any specific leak-detection instrumentation, or at most, detectors at a few points believed to be susceptible to leakage. Ordinarily, those responsible for the systems are not greatly concerned about the lack of leakage instrumentation; the justification being: (1) no good leak-detection instrument is available; (2) the system is well designed to minimize the possibility of leakage; and (3) the system is designed so that a leak can be accommodated safely and with acceptably low equipment damage or loss of data or operating time.

In larger systems, complete leak-detection coverage is the usual objective, but is not attained. It is recognized that most of the instruments have a very limited range of successful operation, hence an approach toward adequate coverage requires the use of several different types. A partial coverage often is regarded as acceptable.

Those responsible for the design and operation of very large sodium systems are much more concerned about leaks and regard the advancement of sodium leak-detection technology as urgent.

Specific leak detection methods and instruments are discussed in the remainder of this report.

2. Sodium Behavior at a Leak

The behavior of leaking sodium determines the applicability of the various detection methods and instruments. The environment of the leaking sodium is the main factor influencing the behavior. The environments involved are

- Gas environment, typified by leakage from components such as pipes and vessels without thermal insulation contacting the surface or close enough to affect the leaking sodium.
- 2) Gas-solid environment, typified by leakage as described above, but with thermal insulation or other material in contact with the surface or sufficiently close to affect the leaking sodium.
- 3) Liquid, typified by leakage within heat exchangers.

a. Leakage Into Gas Environments

The sodium leakage-to-gas behavior depends on leak position, form and size, pressure difference, temperature, and pressure and reactivity of the gas with sodium. The system design and operation establish the temperature and reactivity, hence are controlled factors and are known. The other factors are not predictable.

If the gas is relatively inert so that negligible reaction occurs, and the leak rate is low, i. e., oozes out, the sodium may be expected to run along the surface, drip off, or vaporize. If it runs along the surface or drips off, its presence can be detected by contact sensors placed in the path. If the leaking sodium can be confined so that an accumulation occurs, contact or level sensors can be used. The sodium vaporizes at a rate increasing with temperature so at sufficiently high temperature the sodium may be detected by vapor sensors.

The ease of detection of liquid sodium generally improves with higher leakage rates, so the methods which are based on sensing liquid sodium contact, level, or vapor may be expected to be applicable for higher rates as well as the low rates. A possible exception is in the use of a contact sensor. If the position of the leak is such that the sodium squirts away from the vessel walls, and away from a contact sensor, the sensor is ineffective. The typical remedy for this behavior is the use of baffles or jackets arranged to intercept the stream and direct the flow to a sensor.

In an inert atmosphere the methods based on fire or smoke detection are ineffective unless a material capable of producing the reaction is in the path of the leaking sodium.

If the gas is reactive with sodium, and the leak rate is low (or of an oozing character), a reaction will occur about as fast as the sodium oozes out. The reaction product generally is solid or crusty material formed on the leaking surface. At slightly higher leak rates, the reaction occurs over a greater region. In either case, the reaction products accumulate; the possible results of which are: (1) continued leaking and production of reaction products which flake off; (2) self-plugging of the leak; and (3) inducing corrosion on the container surface thereby engendering a substantially larger leak. The reaction products as described do not operate the contact or level sensors of typical

design and do not produce significant vapor for detection. None of the contemporary sensors respond well to these reaction products; hence, leaks of this type often are undetected until they come to the attention of operating personnel, preferably during maintenance or general surveillance functions.

If the leak rate is high, the sodium will burn if the temperature is high enough and if the gas composition can support burning. The burning produces heat, light, and smoke as the evidence of possible sources of leakage. Several methods of sensing these products are feasible; smoke detectors being the most commonly used instruments.

b. Leakage Into Gas-Solid Environment

To reduce heat loss, it is customary to provide thermal insulation over as large a surface area of the sodium container as is practical. Several forms of thermal insulation can be used. Those most commonly used on sodium containers are blocks, blankets, or cast compositions which are primarily silica or alumina.

The use of thermal insulation is detrimental to substantially all methods of leak detection. Direct viewing is prevented, leakage flow paths are altered, and vapor and smoke are trapped. These problems are reduced by providing openings in the insulation, or space for probes between the container surface and the thermal insulation. Sodium leaking into a region of thermal insulation can behave substantially as described for leakage into a gas atmosphere if the openings and spaces are provided.

If leaking sodium can contact the insulation, some of the sodium may be absorbed. This contact can be detrimental in two ways: (1) the sodium is trapped and not available to actuate typical detectors; and (2) the contact may result in a chemical reaction with the constituents of the thermal insulation and produce corrosive products which further damage the container walls. (24)

A leak in a moderator can is a special case to consider. Such leaks are detected by reactivity measurements: sodium entering and soaking the moderator (graphite) causes a decrease in reactivity. Experience in detecting several moderator can leaks has demonstrated the reliability of this method, even to the point of predicting the approximate ring location. (25)

c. Leakage Into Liquid Environment

Sodium leakage into a liquid environment can occur in heat exchangers and in systems surrounded by a liquid. In intermediate heat exchangers (sodium-to-sodium) the nature of the leak does not greatly influence the leakage behavior, and the methods of detection are not greatly dependent on these factors. Since the environment on the leaking surface generally is not corrosive, progressive damage and leakage is not to be expected. For this reason, and because of other conditions involved in intermediate heat exchangers, the prompt detection of a small leak of nonradioactive sodium is not critical. The sodium environment precludes the use of most leak-detection methods commonly used in the gas environment; consequently, the choice of methods is relatively small.

In sodium-to-water heat exchangers, or steam generators, the pressure on the water side is much greater than the pressure on the sodium side during normal operation; hence, sodium leakage would be a freak event if a leak occurred. (The usual direction of leakage is from water into sodium.) The nature of the leak does not greatly influence the leakage behavior, and the methods of detection are not greatly dependent on these factors. The environment is corrosive in the region of a leak; therefore, progressive damage and greater leakage is to be expected. The water environment precludes the use of most leak-detection methods commonly used in the gas environment; consequently, the choice of detection methods is relatively small. A conventional analyzer, responsive to sodium in the steam system, can be used.

III. INSTRUMENTS FOR DETECTION OF SODIUM LEAKAGE

The operation of most contemporary instruments for leak detection significantly depends on the form of the leaking sodium. Therefore, the instruments are discussed in terms of form of sodium and the nature of the response.

A. LEAK DETECTION BY SENSING LIQUID SODIUM

Instrumentation based on contact with the leaking liquid sodium is most effective when used in the gas environment. Any solids present can interfere with the leakage flow and retard or prevent flow to the sensor. The liquid contact methods are not applicable to detection of sodium leaking into another liquid metal.

The types of instruments which function by liquid metal contact or proximity are those based on: (1) electrical circuit methods; (2) thermal methods; and (3) volumetric or level methods.

1. Electrical Circuit Methods

Leaking sodium can be detected by its action on an electric circuit as described in the following techniques.

a. Sodium Providing Electrical Contact

In this method, electrodes are placed in the expected path of leaking sodium, and when a quantity of sodium is sufficient to contact both electrodes an electric current can flow to the indicator. One of the electrodes may be the containment structure and the other may be a wire or rod in close proximity. However, a separate pair of electrodes usually is preferred. (26) To monitor an extended region, an array of electrodes, or a pair of wires is used.

Despite its simplicity, three factors limit the success of this method:

1) Electrode and insulator compatibility. The electrode and insulating material should be compatible with leaking sodium and its reaction products to avoid deterioration and possible signal reduction or loss during contact with leaking sodium, and to reduce the factors which may require electrode and insulator replacement in restoring the system after a leak.

- 2) Electrode spacing. The electrode spacing determines the amount of sodium needed to bridge the gap and close the electrical circuit. For best threshold response time, the gap should be small. However, the minimum spacing is limited by the possibility of an inadvertent short circuit caused by mechanical shifting of one or both electrodes. A well-designed mechanical support with a close spacing provides a fair solution to the problem. Consideration of thermal-expansion-induced shifting as well as the other mechanical forces is required.
- 3) Detoured leak. Several conditions can occur to cause a leak to follow a path other than the one leading to the sensor. For example, sodium from a small leak anywhere on a pipe may be expected to flow along the circumference to the lower surface and drip onto a sensor. However, several factors, such as the orientation, shape, and size of the hole, may cause the sodium to squirt away and never follow a path to the sensor.

There are two common forms of short-circuiting sensors which depend primarily on optimum placement for their operation. One consists of two parallel wires positioned by two-hole ceramic spacers shaped to assure exposure of the wire surface. Stranded constantan wire has been recommended in early reports. (26) The wires are positioned where they are most likely to be contacted by leaking sodium; generally, on the lower surface of the containment vessel. However, sometimes the wires are wrapped around to cover a substantial area.

Some users find this method of detecting leaks to be satisfactory, but more report it to be unsatisfactory. The most specific complaints relate to accidental shorting with the consequent false alarms, and failure to indicate a leak because of detoured leakage paths. This method is known to be in use in a few installations but its usage is not prevalent.

Another form of short-circuiting sensor uses two wires positioned by weaving them into a fabric tape. (27) The required wire characteristics described for the ceramic bead-spaced type are applicable. The fabric tape must be capable of withstanding the environment without disintegration or impaired insulating properties which can cause false alarms. The disintegration of some fabrics

at high temperature apparently is acceptable if the thermal insulation or other material provides wire support. The tape usually is made of a ceramic fiber material. While the use of the fabric tape may offer some advantages in the mechanical positioning function, the tape fabric inhibits sodium penetration to the wires, resulting in a delay or failure to indicate a leak. A loose weave should permit better penetration.

Reports on the performance of the tape-type sensor in operational systems are lacking. It was described in early literature but no evidence of present day usage has been found. (26,27)

The probability of getting the liquid sodium to the electrodes, as described above, appears slight. The probability is greatly enhanced by providing some form of liquid collector.

There are two general forms of collectors: an open basin type, and a jacket type providing complete enclosure.

The basin technique involves placing a liquid-collecting surface under the surveillance region of the containment structure so that any sodium dripping from this region is channeled to the liquid sensor. Most of the commonly used liquid metal level sensors could be used, (28) but the discrete point type is the most appropriate and generally used. The commonly used forms are the electrical contact type, which operate in essentially the same manner as described in the previous section. The general requirements regarding mechanical stability and compatibility are the same.

The sensor, placed in the collection vessel, consists of either: (1) an electrode rod and collector basin; or (2) a pair of electrode rods, so that liquid sodium contacting the electrodes closes and actuates the electric circuit. The basin is designed to collect dripping sodium over the desired surveillance area and to channel, with minimum delay, as much of the liquid as possible into the sensor region. The sensor is designed for best threshold response, consistent with reliable operation, and freedom from spurious signals caused by accidental contact resulting from mechanical shifting of the electrodes.

The suitability of this method depends on the basin catching the leaking sodium and the sodium closing the electrical circuit. These conditions are

readily met in some instances. An example of failure is in the case of a leak on a side or upper surface so that the leaking sodium squirts beyond the basin. A common remedy for this situation is the use of side walls, or a foil or thin metal envelope to intercept the sodium stream and direct it to the basin. (28)

The collector design should provide a path to the sensor with a minimum obstruction and should have a sufficient temperature to maintain the sodium in the liquid state. There are objections to this since maintaining the sodium in a liquid state in an open basin is contrary to safety objectives.

Some of the problems encountered with the open-basin method are mitigated by the use of a closed jacket for collecting the leaking sodium. One method (29) which has been used is illustrated in Figure 1. The jacket may be added to the component specifically for the purpose of collecting leaking sodium or it may be a part of the component adaptable to this function. Ordinarily, any thermal insulation is placed outside the jacket so that leaking sodium does not contact it. The disadvantages of contact, which are reduced leak-detection response and the formation of corrosion compounds, have been discussed.

A jacket surrounding the sodium container assures collection of all leaking sodium regardless of the nature of the leak. However, the use of a jacket does not assure the delivery of all leaking sodium to the sensor. Sodium may react with materials it contacts and form compounds which are not readily detected by a sensor responsive to liquid sodium. Also, some sodium may be retained on the jacket surface or in crevices so that the initial quantity of leaking sodium may never reach the sensor. This aspect is especially significant where the distance from the leak to the sensor is long. These factors show the improbability of detecting a small leak.

The typical construction of a few components includes an enclosure or jacket which may be used to aid in leak detection. The bonnet surrounding the bellows of a bellows-sealed valve is an example. For such valves, it has become common practice to insert a simple electrode into the enclosure through the vent hole. The electrode is often made of a length of two-conductor sheathed thermocouple stock having the two wires suitably exposed. Sodium leaking through the bellows fills the surrounding cavity and contacts the sensor electrodes.

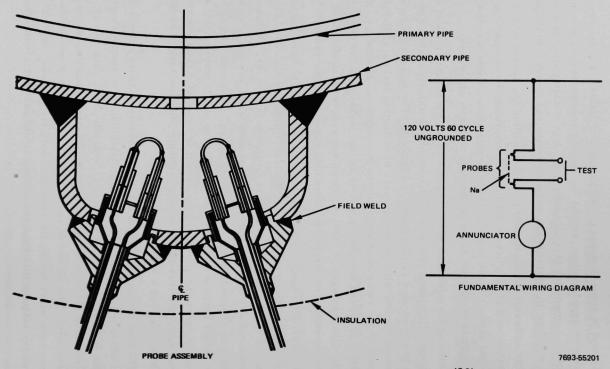


Figure 1. Leak Detector Probes Enclosed in a Jacket (29)

Reports on the performance of the sodium collector-type leak detectors vary. It appears that the simple open-basin type is fairly satisfactory. Some reports indicate satisfaction with the jacket type, while other indicate some problems. There is general agreement that the technique described for monitoring bellows-sealed valves is satisfactory.

In the electrical contact methods, an alternating current rather than a direct current ordinarily is used. The choice usually is based on the availability and convenience of an alternating current rather than any specific technical factor. One technical factor which can be cited is that a direct current can cause the deposition of insulating layers on the electrode surface. In such an event, the initial, leak-alarm signal may decay to a useless magnitude as the deposition process proceeds. This behavior will not occur when alternating current is used; hence, a sustained signal may be expected. In many alarm circuits, a sustained signal is not required to maintain the alarm. However, it is advantageous to have the sustained signal available. One reason is to enable checking for false alarms such as those caused by moisture.

b. Sodium Impairing Electrical Insulation, Permitting Electrical Contact Between Electrodes

The electrode assembly can be designed so that the electrodes make contact directly if the separating material or insulation is dissolved by the action of the leaking sodium. Satisfactory operation depends on the integrity of the insulation in the absence of sodium, the speed and effectiveness of the insulation removal by sodium, and the quality of the electrical contact.

No record of the use of this method could be found; however, an examination of the feasibility and preliminary tests of one design has been reported. (30) Its operation is based on the destruction of the insulating film on anodized aluminum. In one form, a grid of anodized aluminum wire is used. The resistance between the intersecting wires is measured; a significant decrease being indicative of failure of the insulating film at the intersections. Tests on a model having 2.54 mm spacing of the wires readily detected 20 to 50 mg of hot sodium falling onto the grid.

c. Sodium Providing Electrical Capacitance

The detection techniques described above can operate only when electrical conduction is achieved. Another method of operation is possible based on the

change in electrical capacitance of the electrode circuit caused by the presence of the sodium. Sodium contact, or at least electrical dc conduction, is not involved; therefore, such problems as the conversion of the leakage material to a poorly conductive reaction product are avoided. This method is applicable to the electrode systems described, but requires an alternating current. In general, the capacitance increase due to the presence of leaking sodium is small; therefore, the alternating current frequency must be rather high. The frequency required depends on the capacitance change which is a function of the leakage mass and electrode geometries, the relative positions, and the permittivity of the dielectric materials involved.

No reported application of this method was found. The concept is sound, and a model can be postulated in which satisfactory operation appears certain. However, the practical problems involved with the high frequencies required make it doubtful that this technique would be feasible for sensors using long wires to "cover" a substantial area. However, for point sensors the problems are fewer and the method appears attractive to the extent that electrical dc conduction is not required.

d. Sodium Breaking Electric Circuit by Dissolving Wire Conductor

Sodium leakage can be detected by its action in opening an electric circuit. The feasibility of this method is postulated on the highly reactive nature of sodium and reaction compounds which have the ability to dissolve or corrode several metals. The sensor consists of a wire of such a metal placed so that the leaking sodium contacts it and the reaction destroys the wire continuity. Since the wire is part of an electric circuit, the loss of continuity stops the current flow, thereby signaling a leak. Many of the factors discussed in the circuit-closing type are involved in the circuit-opening type. Hence, the usefulness is not significantly different. The response of the wire to the sodium may be improved by passing enough current through it to raise its temperature. This is particularly applicable to wires of the noble metals which, in general, are soluble in sodium. Other metals, such as copper, may be sufficiently soluble in sodium, but the high temperature may cause the formation of surface films which have an adverse effect.

No reported use of this method could be found. Conditions can be postulated in which a detector based on this technique may be satisfactory. However, the general applicability is doubtful. In addition, response time may be poor.

e. Thermal Methods

Thermal contact of leaking sodium with a thermal sensor can be used as the basis for a leakage indicator. Good thermal contact is advantageous but the contact requirements are less stringent than those for the electrical contact method. The disadvantage of the thermal method is that the useful property, heat transferred from the sodium in indicating its presence at the sensor, is negligible for very small leak rates and may be negligible in other circumstances. This is because operation of the thermal detector requires the leaking sodium to transfer enough heat to the sensor to raise its temperature a significant amount above the sensor ambient temperature. In typical circumstances, leaking sodium may lose so much heat to its surroundings in its travel to the sensor that the sodium-to-sensor temperature difference will be small, hence the signal will be small. This method may be feasible in circumstances in which the required thermal conditions can be met. The sensors may be used in the manner described for electrical circuits, i.e., point sensors mounted in drip pans or other sodium receptacles, or may be distributed as indicated for wire sensors. A conventional thermocouple is an example of a thermal sensor for point detection service. For monitoring a line or an area, a special form of thermocouple can be used. This consists of a cable containing a pair of thermocouple wires insulated by an insulator having a negative resistivity temperature coefficient. A high temperature at any point or region along the length decreases the resistance of the insulation at the point to a low enough value that the point becomes a thermocouple junction.

The use of thermal sensors for leak detection appears negligible, and possibly is nonexistent. This method is probably restricted to special circumstances; it does not appear to have general applicability.

f. Volumetric or Level Methods

Leaking sodium which is channeled to a reservoir can be detected by a liquid sodium level gage in the reservoir. The various aspects of this method were discussed in a previous paragraph where the attention was limited to

simple electrical contact sensors. The resistance-tube type is the only kind of level gage, other than the discrete-point electrical contact type, which is known to be used for leak detection. The resistance-tube type is not common either. No advantages are apparent in the use of level gages other than the simple, discrete-point electrical contact level gages.

B. LEAK DETECTION BY SENSING SODIUM VAPOR

Sodium leakage into a gas, or gas-solid environment, produces sodium vapor as well as liquid sodium and solid reaction products. The behavior of a vapor, especially its diffusability, is significantly different from a liquid or solid. The dominant shortcoming of the liquid detection methods, as discussed in the previous section, is the possibility that the leaking liquid may not always reach the sensor. However, the diffusability of a vapor assures its reaching the sensor unless specific impediments are imposed.

A number of factors limit the success of leak detection by sensing vapor:

- 1) Impediments to Vapor Formation. The quantity of sodium vapor formed is a function of the ambient pressure, and the sodium temperature and impurity content. Analysis shows that the amount of vapor which can be expected from low-temperature sodium is relatively small. The amount of vapor which can form is greater in a low ambient pressure. Reducing the ambient pressure as a means of increasing vapor formation is impractical, except possibly in small enclosed systems.
- 2) Chemical Reaction of Vapor. Contact of sodium vapor with many substances results in the formation of sodium compounds, and a consequent loss of sodium vapor. The most common cause of such a loss is through reaction of the vapor with oxygen and moisture in the atmosphere. In installations where the leakage is into an unenclosed region of typical atmosphere, all the vapor may be expected to react. In such a region, sensors which respond only to sodium vapor may not be expected to be effective. However, it is possible to provide regions of isolation, such as by ducts, so that the vapor contact with the atmosphere will be minimized. A complete enclosure of the system, providing a limit on the supply of oxygen and

moisture, improves the feasibility of vapor detector use since a relatively small quantity of sodium can deplete the supply of oxygen and moisture, leaving an effectively inert atmosphere. Subsequent production of vapor by leakage may be sensed by vapor detectors.

When the vapor reacts with oxygen and moisture, smoke is produced. The smoke is essentially particles of sodium oxide. Smoke behavior and characteristics are similar in some ways to vapor but there are distinct differences. Some sensors can respond to either, others cannot. Since smoke is a reaction product, its detection is treated in III.C.1.

The vapor concentration may be reduced by reaction with solid materials, such as some of the constituents of thermal insulation.

- 3) Condensation of Vapor. Sodium vapor will condense when the temperature of the gas is reduced below the sodium dewpoint. If a cold surface is present, some sodium will condense on the surface and eventually, significant quantities of sodium can accumulate there. This decreases the amount of vapor available to actuate a detector. If sodium vapor is cooled rapidly, a fog will form which will not readily coalesce. Such a fog can be transported for a considerable distance by a carrier gas.
- 4) Ambient Gas Disturbances. Vapor paths and the concentration at the sensor are very susceptible to gas currents such as caused by ventilation or convection. However, this can be an advantage if the sensors are placed in the ventilating ducts since the vapor concentration there will be increased. In an outdoor installation, vapor detection is practical only if the vapor path is protected. Unless some protection is provided, vapor issuing into the atmosphere soon oxidizes and becomes smoke which readily blows away in slight atmospheric disturbances or wind.
- 5) <u>Diffusion</u>. The concentration of a vapor at a sensor may be a function of its distance from the source, in the absence of directive devices such as ducts. In the case of steady flow, the relation is the consequence of geometrical factors. In the case of a point source, the

usual situation for a small leak, the concentration varies inversely with the square of the distance from the source. For a line source, the concentration varies inversely with the distance for distances substantially less than the line length. For a surface source, the concentration is independent of distance for distances substantially less than the surface dimensions.

The types of instruments which function by response to sodium vapor are based on the methods of: (1) analytical chemistry, (2) light emission, and (3) light absorption, which is generally known as atomic absorption.

1. Analytical Chemistry Methods

In the analytical chemistry methods, the vapor is drawn into a reagent which responds to sodium. Well-known analytical techniques can be used.

An analytical system has been described $^{(31)}$ which uses a sampling tube to carry the vapor from the region under surveillance to a detector consisting of an indicator solution. An inert gas such as N_2 is used as a carrier. Thymol blue has been used as an indicator. Concentrations as low as 2.3×10^{-4} gm of Na per cubic meter of N_2 may be detected. This method is not considered practical for temperatures below about 250°C. Experiements have shown that the vapor may be carried in N_2 at room temperature through 1/4-in.-OD tube for distances as great as 10 m without loss resulting from condensation.

No published data are available on the performance of this method in operating systems.

An electrical conductivity cell is a more convenient indicator than the thymol blue since an electrical signal is provided. In this method, the sample of air is drawn from the region under surveillance and the air is bubbled through pure water. Any sodium in the air sample will react with the water and produce several reaction products, which results in an increase in the ionic conductivity. To minimize the possible effects of environmental variations causing conductivity changes, a pair of identical cells are exposed to the same environment but with sample air bubbled through only one cell. The two cells are connected to the electrical circuit so that an imbalance created by a change in conductivity of one, produces a signal. The concentration of sodium in the cell is a function of the sodium concentration in the air and the length of time the mixture is

bubbled through the water. Consequently, the threshold sensitivity increases with bubbling time.

The analytical technique described above is applicable to detection of smoke as well as vapor, since sodium smoke will produce an easily detected reaction in a conductivity cell.

2. Light-Emission Methods

In the light-emission method of analysis, the substance is excited to produce radiation characteristic of itself. The radiation wavelengths are indicative of the identity of the atoms producing the radiation, and the intensity is indicative of the concentration. In general, the sensor, typically a photoelectric cell, has a relatively broad wavelength response, so the wavelength is determined by passing the light through a monochrometer to resolve the wavelengths. The sensor output signal amplitude indicates the radiation intensity. The possible means of excitation include: flame, radio frequency, arc, spark, X-ray fluorescence, and neutron activation. The most common form of excitation, and the only form used for sodium leak detection, is the flame. This technique is commonly known as flame photometery. Sodium is easily ionized in a flame, emitting a characteristic yellow light, the principal radiation being at 5.89 x 10⁻⁷ m. The wavelength resolution requirements for leak detection generally are not rigorous; therefore, an instrument of considerable simplicity compared to the typical analytical instrument is satisfactory. The flame will decompose sodium compounds; hence, the flame method will be effective in detecting smoke which is essentially particles of sodium oxide.

Instruments for detecting sodium vapor are proven and commercially available. They are very sensitive, having a threshold limit of 5×10^{-3} gm of Na per cubic meter of air.

An open flame is generally regarded as undesirable and its use as a means of excitation may be particularly undesirable for sodium leak detection. Also, the possible undesirable problems associated with combustion products may be a disadvantage of this method. Radio frequency excitation has been considered as an alternative to the open flame but this technique is not sufficiently developed for immediate use.

3. Light Absorption Methods

In the atomic absorption method of analysis, the substance, in an unexcited or ground state, absorbs radiation of specific wavelengths characteristic of itself. The wavelengths are those which are produced when the substance is excited. In general analysis, a wide range of wavelengths is required. However, for a specific substance, as in the case of sodium vapor, a sodium lamp provides the required wavelengths. The method of detection is relatively simple, at least in principle. Light from a sodium lamp traverses the region containing the vapor and passes to a light sensor, typically a photoelectric cell. The amount of light absorbed is a function of the vapor concentration and the path length through the vapor. Generally, some form of zeroing or checking circuits are added.

If the vapor reacts chemically, forming sodium compounds, oxide, or smoke, for example, the light will be dispersed by the particles; the result being an intensity reduction at the sensor.

In one design, $^{(32)}$ a light beam from a low-pressure sodium lamp traverses the region under surveillance to an optical detector cell (CdS). The threshold limit of sensitivity is 75×10^{-6} gm/m³. This instrument is reported to perform well when the leak is in the vicinity of the light beam. For large or complex systems the use of a number of instruments to cover the region is recommended. Figure 2 is a schematic diagram of this kind of detector.

Another technique $^{(33)}$ uses sampling tubes to convey the vapor from the region under surveillance to the optical instrument. The sodium vapor may be carried entrained in an inert gas over substantial distances, as indicated in a previous paragraph. This technique is capable of detecting concentrations as low as about 35×10^{-6} gm/m 3 .

The atomic absorption method has been described in several reports investigating the feasibility of leak-detection methods. Bench-test data have been presented, but no evidence of the use of this method in operating systems has been found.

4. Leak Detection by Radioactivity Sensors

When natural sodium Na²³ has been activated, forming Na²⁴, the strong gamma radiation from the sodium provides an additional means of detection:

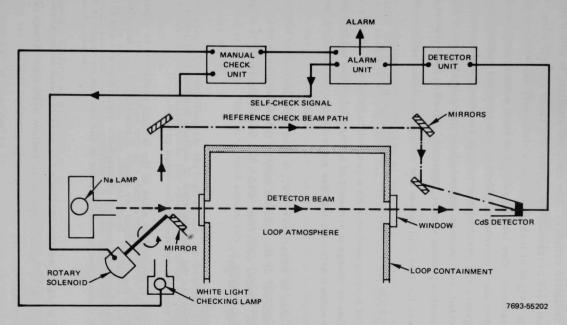


Figure 2. Schematic Diagram of an Optical Sodium Vapor Leak-Detection System(32)

the use of gamma radiation sensors. The common situation in which Na²⁴ is formed is in sodium used to transfer heat from a nuclear reactor core. The radioactive sensing method of leak detection is commonly used for the primary loop of a nuclear reactor. Any leak results in at least a trace amount of vapor or smoke released to the atmosphere. Since a loop carrying radioactive sodium (or the primary system of a reactor) normally is enclosed, and controlled forced ventilation is provided, the common method of sampling is to monitor the exhaust atmosphere with a gamma sensor, typically placed in the exhaust dusts.

Gamma sensors for this application are readily available commercially.

C. LEAK DETECTION BY FORMING AND SENSING A REACTION PRODUCT

The reaction of leaking sodium with a reagent to produce a readily sensed reaction product, or to change a property of a material contacted by sodium, provides a means of leak detection that has some merits not found in the other methods.

The reaction may be intentional, i.e., a specific material or additive is selected and introduced, or the reaction may be the consequence of the typical materials present. Smoke detection, which has been discussed, is a familiar example in the latter category.

1. Smoke Detection

Smoke may form as the consequence of sodium burning as it leaks, or in the conversion of vapor to smoke as discussed earlier.

Smoke detection is limited by some of the factors pertinent to vapor; these are: (1) the need for the conditions for smoke formation, i.e., moisture and oxygen in the atmosphere; (2) ambient atmosphere disturbances; and (3) diffusion. The discussion of disturbances and diffusion in the section on vapor is applicable to smoke.

A number of smoke detection methods are possible and some have been used for leak detection in several operating sodium systems. Also, some of the vapor detection instruments can respond to smoke.

Smoke also is amenable to detection by means of an optical method similar to that described for vapor detection. The operating principle is somewhat

different in that the light traversing the smoke is scattered rather than absorbed. The wavelengths in the light are not significant. The limit of sensitivity is of the order of 1.5×10^{-3} gm/m³.

Commercial smoke detectors are used in a number of sodium installations. (34)
Their rather widespread usage probably is due to their commercial status,
availability, and ease of installation, rather than demonstrated performance as
a sodium leak detector. No substantial body of performance data on the smoke
detectors has been published, but oral reports indicate disappointing performance
in some cases.

One technique used is based on the change in current in an ionization chamber as the result of smoke particles. Two identical ion chambers are used. They are connected in a balanced electrical circuit, and placed so that both are in a similar environment; but one is exposed to the sampling region and the other is protected from smoke. A voltage is maintained across the electrodes and an ion current is maintained by an alpha emitter (a minute amount of radium). The presence of smoke particles in the exposed chamber reduces the current flow and this actuates the electronic circuits. False alarms may be caused by changes in ambient conditions and by the detection of dust or other particles not related to a leak. The threshold sensitivity is about 0.1 gm of sodium per cubic meter of air.

The system of bubbling air through water, as described earlier, is applicable to smoke detection also since the smoke dissolved in water increases the ionic conductivity.

Another method makes use of a dual-compartment jacket around the component under surveillance. One compartment contains a gas which, when reacting with leaking sodium, produces a smoke that is carried through a tube to a smoke sensor. (35)

2. Specific Chemical Reagents

One of the main difficulties with conventional leak-detection techniques is in getting the leaking sodium to the sensor. Some success in circumventing this problem has been achieved by using a specific chemical reagent which, upon reacting with leaking sodium, produces a readily detectable reaction

product. This system requires: (1) a reagent which can be suitably dispersed in the region under surveillance so that any leaking sodium will contact it; and (2) a reaction product which readily reaches the sensor and is readily detectable.

The reaction of methyl alcohol with sodium to produce hydrogen is an example of this technique which was developed to detect leaks at temperatures below the range of successful operation of vapor detectors. Although developed for a NaK system, ⁽³⁶⁾ it is applicable to sodium systems. The ambient atmosphere consists of an inert gas that contains some methyl alcohol vapor. The alcohol vapor reaction with leaking sodium produces hydrogen, a product easily detected by means of proven commercial sensors. The method was reported to be satisfactory in bench tests, but the lack of leaks during use on a system prevented a complete evaluation.

Methods based on adding a specific reagent to form a reaction product have not been developed or even considered to any significant extent except in the one case mentioned above. The concept is worthy of further consideration directed toward creating a surface coating which contains a suitable reagent. The coating could be in the form of a paint to be applied to the sodium container, or a specially designed thermal insulation.

3. Sodium-Sensitive Materials

In addition to the generation or release of a specific reaction product to be detected, some methods have been considered in which the reaction produces a change in a material quality or property. For example, sodium-induced deterioration of insulation between two conductors in an electrical circuit has been considered. One form, based on the use of anodized aluminum wires placed in mechanical contact, was described earlier. Sodium contacting the anodized surface destroys its insulating properties, resulting in a shorting of the aluminum wires which are connected in an electric circuit.

Methods based on this concept have not been developed except for the one case mentioned, no substantial effort has been directed toward these techniques; however, they are worthy of further consideration.

D. SODIUM LEAKAGE INTO A LIQUID

Detecting a leak in a wall by permitting contact or mixing of the sodium with a liquid outside, depends on the nature of the external liquid. Most of the

techniques described for leakage into a gas atmosphere cannot be used to detect leakage into a liquid. Two cases are of interest: sodium leakage into sodium (or another liquid metal); and sodium leakage into water.

1. Sodium Leakage Into Sodium

In an intermediate heat exchanger, with sodium on both sides of the separating wall, the number of factors indicative of a wall leak are relatively small. An increase in the quantity of sodium in one system and a corresponding decrease in the other system, and shown by level or pressure gages, can provide a leak indication. Also, if the primary sodium is radioactive (which is usual when it is heated by a reactor), and the secondary sodium is not radioactive, radiation monitors in the secondary can provide an indication of a leak from the primary to the secondary.

Sodium-to-sodium leak detection generally has not been of great concern. The ease of detection, when one system is radioactive, obviates the need to search for better methods. Furthermore, the leaking region is not exposed to corrosive action as in the case of the sodium-to-air leakage where cumulative self-propagating damage makes detection urgent.

2. Sodium Leakage Into Water

In ordinary steam generator operating conditions, pressure on the water side is much higher than pressure on the sodium side. Consequently, except for unusual circumstances, the direction of leakage is from water into sodium, a subject not treated in this report. Sodium leakage into water can be detected easily by well-established practices using commercial water analyzers which are responsive to sodium.

REFERENCES

- F. L. Mangold and R. A. Tidball, "Sodium Leak Detection and Insulation Tests," Mine Safety Appliances Co., TR-XIII (March 1954)
- F. L. Mangold and R. A. Tidball, "Report II on Sodium Leak Detection and Thermal Insulation Tests," Mine Safety Appliances Co., TR-17 (November 1952)
- W. Milich and E. C. King, "Sodium Leak Detection and Thermal Insulation," Mine Safety Appliances Co., Memo Report 41 (August 1953)
- 4. W. Milich and E. C. King, "Sodium Leak Detection on Vertical Piping," Mine Safety Appliances Co., TR-34 (November 1954)
- F. L. Mangold, "Sodium Leak Detector Preliminary Report 1," Mine Safety Appliances Co., Memorandum Report No. 4 (February 1952)
- 6. Progress Report 25, September 1962, "Effect of 1200°F Sodium on Austenitic and Ferritic Steels," MSAR 62-126 (October 19, 1962) pp 10, 26, 28
- 7. Quarterly Progress Report, January-March 1966, "Effect of High Temperature Sodium on Austenitic and Ferritic Steels," MSAR-66-71 (April 25, 1966) p 15
- Quarterly Progress Report, July-September 1966, "Effect of High Temperature Sodium on Austenitic and Ferritic Steels," MSAR 66-220 (October 1966) p 9
- Quarterly Progress Report, October-December 1965, "Effect of High Temperature Sodium on Austenitic and Ferritic Steels," MSAR 66-09 (January 17, 1966) p 11
- Quarterly Progress Report, April-June 1965, "Effect of High Temperature Sodium on Austenitic and Ferritic Steels," MSAR 65-96 (August 6, 1965) p 4
- Quarterly Progress Report, October-December 1967, "Effect of High Temperature Sodium on the Mechanical Properties of Candidate Alloys for the LMFBR Program," MSAR 68-14 (January 1968) (Not cleared for publication)
- Quarterly Progress Report, October-December 1966, "Effect of High Temperature Sodium on Austenitic and Ferritic Steels," MSAR 67-17 (February 3, 1967) p 7
- "Review of SIR Project Model Steam Generator Integrity," KAPL-1450, (November 1, 1955) p 23
- Quarterly Progress Report No. 5 March-May 1968," Sodium Components Development Program Mass Transfer Investigations in Liquid Metal Systems," GEAP-5648 (July 1968) p 63

- 15. H. L. Bowers and W. E. Ferguson, "Structural Materials in LASL Liquid Sodium Systems," Nuclear Metallurgy, 9, pp 227-255
- B. E. Farwel and M. F. Parkman, "Status of SNAP 8 NaK Corrosion Program at AGN," AEC-NASA Liquid Metals Information Meeting, Conf. 650411, April 21-23, 1965, pp 121-129
- 17. R. C. Andrews et al., "Topical Report No. 4, Results of Mechanical Properties Tests of 316 SS Specimens in 1200°F Sodium Contaminated with Carbon," MSAR 65-194 (December 1965) p 109
- 18. "History of the AEC Sodium Components Development Program," ORNL-3955, Vol. I, Special (December 1966) pp 196, 211, 229
- "History of the AEC Sodium Components Development Program," ORNL-3955, Vol. II, Special (December 1966) p 501
- 20. "History of the AEC Sodium Components Development Program," ORNL-3955, Vol. III, Special (December 1966) pp 1083, 1152, 1165
- W. T. Lee, "Failure Analysis of an SCTI Sodium Freeze Trap," LMEC TDR No. 69-25 (June 26, 1969)
- R. R. Matthews and K. J. Henry, "Location and Repair of the DFR Leak," Nuclear Engineering 13, 149 (October 1968) pp 840-844
- J. P. Brainard and D. C. Kirkpatrick, "Sodium Leak Studies," LA-4129-MS (May 14, 1969)
- 24. "Fuels and Materials Division Progress Report," ORNL-4390 (May 1969) pp 90-102
- "Sodium Reactor Experiment Power Expansion Program, Reactor Safety Analysis Report," NAA-SR-9516, Rev. Special (November 1964) pp VIII-19
- 26. C. B. Jackson, ed., Liquid Metals Handbook, Sodium-NaK Supplement, TID-5227 (July 1955) pp 121-125
- 27. "Instrumentation and Controls Conference, May 1958," ORNL-2695 (April 1960) pp 93-97
- 28. C. C. Beusman, "Preliminary Safety Analysis of the Sodium-Deuterium Reactor (SDR)," NDA-84-14 (March 1959)
- 29. "Enrico Fermi Atomic Power Plant," APDA-124 (January 1959) pp 212-216
- 30. A. W. Smith and J. L. Drummond, "An Examination of Some Methods for Detecting Liquid Metal Leaks in D.F.R. Secondary Heat Exchangers," August 1967. (This is an unpublished document; see Part 2 of Appendix B.)

- 31. D. R. Westervelt, "Sodium Leak Detector," NAA-SR-Memo-1163 (November 1954)
- 32. E. Duncombe, et al., "Some Analytical and Process Instruments for Measurements in Sodium," Symposium on Alkali Metal Coolants, Corrosion Studies, and System Operating Experience, Vienna, Austria, November 28-December 2, 1966, Conf.-661110-20 paper SM-85/16, pp 13 and 24
- 33. R. C. Shepard, "A Sodium Vapor Detector Based on the Principle of Atomic Absorption," NAA-SR-TDR-10553 (November 1964)
- 34. J. G. Yevick, et al., Fast Reactor Technology: Plant Design, (The MIT Press 1966) pp 650-651
- 35. A. Bell, "An Improved Leak Detection Unit," Patent No. 765, 239 (U.K.) (January 1957)
- 36. H. L. Henley, "A Method of Detecting the Presence of NaK in an Inert Atmosphere Under Conditions of Ambient Pressure and Temperature," NAA-SR-TDR-11848 (February 1966)

2. An Examination of Some Methods for Detecting Liquid Metal Leaks in D.F.R. Secondary Heat Exchangers

United Kingdom Atomic Energy Authority

THE REACTOR GROUP

TECHNICAL MEMORANDUM

AN EXAMINATION OF SOME METHODS FOR DETECTING LIQUID METAL LEAKS
IN D.F.R. SECONDARY HEAT EXCHANGERS*

by

A.W. SMITH AND J.L. DRUMMOND

Issued with the approval of Dr. J.S. Broadley

SYNOPSIS

A brief description is given of methods that could be used to detect a sodium leak from the D.F.R. secondary heat exchangers. Those methods that have been examined in the laboratory and on the heat exchanger cubicles are described in more detail.

DOUNREAY EXPERIMENTAL REACTOR ESTABLISHMENT DOUNREAY CAITHNESS

August, 1967.

^{*} This report is an unpublished paper by A. W. Smith and J. L. Drummond, UKAEA, and makes no specific recommendations. This report is not intended to be used for reference and is not available from British sources.

CONTENTS

	Page
INTRODUCTION	1
SODIUM LEAKS INTO AN AIR FILLED BOX	1
TYPES OF SODIUM LEAK DETECTORS	1
Minerva Flame Photometer pH and Conductivity Detectors Ammonia Release Detector Atomic Absorption Detector Light Absorption Detector Light Emission Detector Anodised Aluminium Wire Grid	1 2 2 3 4 4 4 5
DISCUSSION	5
CONCLUSIONS	6
ACKNOWLEDGMENTS	7
REFERENCES	7
TABLES I to III	
FIGURES 1 to 3	

INTRODUCTION

- 1. In 1966 a leak of sodium/potassium alloy was found from one of the secondary heat exchangers of D.F.R. Examination showed the alloy had been escaping for several days and had formed a block of alkali metal carbonate/hydroxide below the leaking heat exchanger.
- 2. Although the liquid metal had escaped there had not been a large fire. The alkali metal had apparently oxidised slowly, but some corrosion was apparent. The corrosion could, in time, have caused a catastrophic failure of either or both the sodium filled pipes and the steam pipe.
- 5. The early detection of a sodium leak is therefore very important. In this report, possible methods are surveyed, and some preliminary experiments are described to compare some of these methods. Flow and level detectors in the liquid metal circuit are not considered here. Emphasis is given to the detection of sodium leaks; it is believed that the results apply equally to sodium/potassium alloy.

SODIUM LEAKS INTO AN AIR FILLED BOX

- 4. So far as is known there is no information on the behaviour of liquid sodium, leaking into air at 150-200°C. Most of the envisaged sodium leak detectors, including a commercially available one, depend upon the presence of sodium oxidation products in the air but it appears that the leak occurring in the D.F.R. circuit did not produce significant amounts of sodium oxide 'smoke', and this type of detector might not have 'seen' the leak.
- 5. Some brief experiments were carried out to see how hot sodium behaves on escaping into hot air. The results, which are only a general guide, are shown in Table I.
- 6. These results confirm that small leaks can occur without a fire occurring. Leak detectors can therefore be conveniently divided into those that will and those that will not detect slow, non-burning, sodium leaks.

TYPES OF SODIUM LEAK DETECTORS

- These are shown in Table II. The table is not exhaustive but does cover the most attractive types for use in the heat exchanger cubicles.
- 8. Each type of detector is now described in detail and consideration is given to its performance and cost.

MINERVA

Principle of Operation

9. The Minerva smoke detector consists of two ion chambers, one in the air to be sampled and the other partially isolated but still exposed to ambient temperature and pressure. A permanent DC voltage of about 200V is maintained across both ion chambers and an ion current is maintained by an a source in each chamber. The two chambers are arranged so that any change in ion current in the one exposed to the air to be sampled causes a trigger valve to operate a relay which rings an alarm. A reduction of current in the detector chamber is caused by presence of particulate matter in the air which reduces the electrons carrying the current.

Performance and Cost

- 10. The method is non-specific and is sensitive to temperature and flow changes. In its present form, the maximum sensitivity at which it can be operated satisfactorily is limited by the onset of false alarms, caused by fluctuations in the ambient conditions.
- 11. In tests on a heat exchanger cubicle, a Minerva detector did not detect 0.1g of sodium, sprayed as sodium carbonate solution, or 1g of sodium, burnt in the bottom of a heat exchanger cubicle. It did detect the smoke from the combustion of 4g of sodium using an air flow of about 3 litres/min. of air past the detector. Thus if we assume that the total volume of air in the cubicle is 1,000 cu. ft., or 3×10^4 litres, and that the sodium oxide smoke is evenly distributed in this volume, then the detection level of the Minerva is about 10^{-4} g of sodium per litre.
- 12. The instrument costs £20 for each head, two probably being needed per cubicle. Instrumentation should be fairly simple and not too expensive.

FLAME PHOTOMETER

Principle of Operation

13. When readily ionised compounds such as the salts of sodium and potassium are passed through a hot flame the metal ions are excited and emit light of specific wavelengths. The intensity of this light can be measured with a photocell and by using filters the measurements can be made specific for each metal. It should be possible to compensate for high concentrations of sodium in the air due to spray from the sea.

Performance and Cost

- 14. A simple apparatus used for tests on the heat exchanger cubicle is shown in Figure 1.
- 15. In tests carried out in parallel with those on the Minerva, it easily detected both the smoke from 1g of burning sodium and 100 mg of sodium as the carbonate sprayed into the bottom of a heat exchanger cubicle. Thus, if we assume that the total volume of air in the cubicle is 3×10^4 litres, that 100 mg sodium is evenly distributed in this air, and that there is a flow rate of 3 litres/min. into the flame, then the detection level of the flame is less than $3 \times 10^{-6} \mathrm{g}$ of sodium per litre, or less than $10^{-5} \mathrm{g}$ per minute.
- 16. These detection limits for the Minerva and flame are directly comparable, but they may not be absolute, as there is no evidence that the sodium was evenly distributed in the air space.
- 17. The cost to install would not be more than £20 for each burner plus the cost of instrumentation, which should not be excessive. Some device would be required on safety grounds to ensure that the flame is maintained.

PH AND CONDUCTIVITY DETECTORS

Principle of Operation

18. If air from the heat exchanger is contacted with water, the sodium oxide can be concentrated into a relatively small volume of solution, and detected

by measuring a change of pH, or conductivity.

19. In a series of laboratory tests, the air containing the sodium combustion products was cooled and passed over a slow stream of water held on an absorbent paper (see Figure 2). The water passed into a small cell of 1-2 ml capacity in which were placed the probes for measuring pH, or conductivity. The water was continuously siphoned out of this cell so that should any sodium hydroxide, oxide or carbonate be in the air, the probes will quickly show a change in the alkalinity or in the conductivity of the water.

Performance and Cost

- 20. The methods can be made specific for alkalinity i.e. sensitive only to sodium oxidation products. To compare their sensitivities with the other methods of leak detection, we may again assume that the 3×10^4 litres of air contains 1g of sodium, evenly dispersed. With the laboratory apparatus, the maximum air flow was about 1 litre per minute and the minimum water flow about 3 ml/minute. Thus the concentration of sodium in the water would be about $10^{-5}\mathrm{g}$ Na/ml or 4×10^{-4} normal. The solutions will contain carbon dioxide in equilibrium with the air, and the sodium fumes will form sodium carbonate. The pH of $4\times10^{-4}\mathrm{N}$ sodium carbonate solutions is about 9.8, and the conductivity about 30 $\mu\mathrm{mho/cm}$, compared with 6 and about 1 $\mu\mathrm{mho/cm}$ for de-ionised water containing carbon dioxide. Thus it should be feasible to detect 1g of burning sodium under these ideal conditions, assuming 100% absorption of the sodium fumes by the water.
- 21. An installation on a heat exchanger may be designed on a larger scale, but it is unlikely that the ratio of air-flow to water (and hence the sensitivity) can be increased. The air must be cooled, and heat losses may become prohibitive. Evaporation of the water would become more serious. Also the absorber would need constant supervision and maintenance, and the methods cannot be recommended for routine in-cubicle use.

AMMONIA RELEASE DETECTOR

Principle of Operation

22. When an alkali is contacted with an ammonium compound, free ammonia is released, e.g.

$$(NH_{\angle})_2 SO_{\angle} + Na_2 O \longrightarrow 2NH_3 + Na_2 SO_{\angle} + H_2 O$$

If the ammonium compound is placed near the heat exchanger pipework, the ammonia gas can be led away without any danger of losing oxide smoke by deposition on surfaces. The ammonia can be detected in several ways.

Performance and Cost

23. A survey of ammonium compounds suggested that ammonium sulphate was the most suitable material available. Unfortunately at the temperature of the heat exchanger cubicles the amount of ammonia released by the thermal decomposition of the ammonium sulphate is enough to give a high ammonia concentration in the air without the presence of alkaline compounds. This high background ammonia level makes the detection of small increases due to the presence of Na20 'smoke' impossible, and the method has not been explored any further.

ATOMIC ABSORPTION DETECTOR

Principle of Operation

24. American workers (1) have attempted to use atomic absorption spectrometry to solve a similar problem. In principle this is the converse of flame photometry. A beam of sodium light is shone through the flame, in which the contaminated air is consumed. The sodium light is absorbed by the non-excited sodium atoms in the flame, and the attenuation of the beam is measured. The equipment is expensive and fairly elaborate, and from the American work appears to need much attention.

Performance and Cost

25. Meyer and Young (1) expected to detect hundreds of μg of sodium per litre of air. It is unlikely that the method can compete with flame photometry, which is more sensitive for alkali metals (2), and less expensive.

LIGHT ABSORPTION DETECTOR

Principle of Operation

26. If a collimated beam of light is shone through the heat exchanger cubicle, from one side to the other, at any convenient level between the H.E. pipes, the intensity of the emergent beam can be monitored with a photocell. If smoke is formed in the cubicle, light will be scattered, and the photocell response will be reduced.

Performance and Cost

27. The method should give an immediate signal if smoke is produced in the H.E. cubicle. The smoke would be detected as near the source as is practicable, and detection does not depend on the smoke being carried in an air stream to a remote instrument. No air circulation is required, avoiding heat losses. Installation would only require two small holes in the walls of the cubicles. The instrument has no moving parts, and should be simple and inexpensive. Sensitivity has not been tested, but it is believed that the dense smoke from burning less than 1g of sodium should be easily detectable.

LIGHT EMISSION DETECTOR

Principle of Operation

28. When sodium burns, a brilliant characteristic light is emitted. The heat exchanger cubicles are almost light tight, so if light guide tubes were taken from each section of heat exchangers to outside the cubicle this light could be detected with photocells or photomultiplier tubes. The same light guides could perhaps be used for visual inspection of each group of heat exchangers. I" diameter aluminium tubes with a smooth internal surface should be suitable; the in-cell end of the tubes could be fitted with a hemispherical lens for collecting light over a wide angle. By using suitable filters, the photocells or tubes can be made fairly specific for sodium light. This method also should give an immediate signal if sodium burns, and does not require smoke to be carried in a circulating air stream.

Performance and Cost

29. The method has not been tried out in this context, nor has it been costed. Several photocells would be required on each cubicle at a cost of \$\mathcal{L}\$ each, but these could all be connected to the same meter or alarm system. Installation would involve cutting holes through the insulation of the cubicles to take the 1" tubes. The tubes should be demountable for occasional cleaning.

ANODISED ALUMINIUM WIRE GRID

Principle of Operation

- 30. When hot sodium or hot sodium oxidation products come in contact with anodised aluminium wire, the insulation of the anodic film is greatly reduced, or removed completely. If a grid of anodised aluminium wire is placed below the heat exchangers and the resistance is continuously measured between intersecting wires in the grid, the presence of sodium or its oxidation products on the grid can be quickly detected. Alternatively, the detector could be made by wrapping anodised wire round a sheet of anodised aluminium and the resistance between the wire and sheet continuously measured, or two sheets of anodised "expanded aluminium" could perhaps be used.
- 31. A wire grid wound on "Sindanyo" asbestos board was installed in one cubicle after the sodium leak was repaired in 1966, but the wires shifted and touched on heating to the cubicle operating temperature, giving a false alarm. The use of anodised aluminium wire should prevent this trouble as contact between the wires does not matter. It would be preferable to use a more inert support material, since "Sindanyo" reacts exothermically with molten sodium and its oxidation products.

Performance and Cost

- 32. The laboratory version of the proposed detector shown in Figure 3 (with 0.1" spacing of the wires) readily detected 20-50 mg of hot sodium and/or its molten oxidation product which fell onto the grid.
- 33. The cost is difficult to estimate particularly as the lagging would have to be removed from the heat exchangers to install the grids. They would be reliable, need no maintenance and would probably detect those leaks that are so slow that only solid material grows from the heat exchanger. The growing column of material would corrode or abrade the anodic film.

DISCUSSION

- 34. The sensitivities, advantages, and disadvantages of the various proposed leak detection systems are compared in Table III. From this comparison, it is seen that the only system to detect a sodium leak which does not ignite is the aluminium grid system, in which sodium metal or its oxidation product makes contact between two wires to close an electrical circuit.
- 35. The other systems all depend on the sodium igniting. They can be divided into two groups, those which do not require transport of sodium fumes or smoke to the detector by flowing air, and those which do. The former type should be the more reliable, and they give an immediate response.

- 36. The two systems which do not require air-borne smoke are complementary depending on the emission of light by the burning sodium or on the absorption of light from an outside source by the smoke produced. The emission detector is simpler, and should detect occasional flashes of light, such as were observed during the actual leak in 1966, even if the amount of smoke produced is small.
- 37. Of the systems requiring air-borne smoke, flame photometry is the most sensitive and reliable, but it requires a gas supply and a constant naked flame. Careful design and regular attention would be required. Atomic absorption spectrometry is a more complex system, and it appears to have no advantages over flame photometry. The Minerva detector is a less-sensitive alternative which should require less attention. But it is not specific, being affected by temperature and air-flow changes. In the heat exchanger cubicles, there is probably adequate convection mixing to give a representative sample for these three systems, but a lagged air recirculation system would be required to avoid heat loss. Measurement of conductivity change in a water scrubber is not an attractive alternative. In theory it is more sensitive than the Minerva detector, but it would need constant supervision and the heat loss could be prohibitive.
- 38. The most important outstanding factor is to assess the danger of developing a significant sodium leak without the sodium catching fire. The limited results reported in paragraph 5 suggested that this is possible, but very unlikely if the leak rate is greater than about 1g/min. at 300°C.
- 39. During the actual heat exchanger leak, a large amount of sodium/potassium alloy had escaped slowly. There does not seem to have been any prolonged or extensive fire, as there was no marked deposition of smoke on the neighbouring pipework. The nature of the material which was around the heat exchangers suggested that a semi-molten product formed slowly and dripped or fell off gradually. This deposit did activate the detector system installed in the base of the cubicle, closing an electrical circuit between two contacts. This is the same principle as the anodised aluminium grid system proposed in this paper, and it gives confidence that such an improved detector in closer proximity to the heat exchanger pipework would be effective.
- 40. Occasional flashes of light were seen during the actual heat exchanger leak and were taken as proof that sodium was leaking. Again, this gives confidence that a permanently installed light-detector would be a significant improvement for leak detection over casual direct observation.

CONCLUSIONS

- 41. If it is essential to detect slow leaks of sodium which may not ignite, the only possible known method is to allow the leaking material to make contact between two wires, preferably of anodised aluminium.
- 42. If it is considered adequate to detect leaks which do ignite, the best method is to detect the light emitted by the fire, since this does not depend on carrying the oxide fumes to a detector.
- 43. Of the air-borne oxide detectors, flame photometry is probably the most sensitive and reliable method, but the Minerva smoke detector would probably be easier to use.

ACKNOWLEDGMENTS

44. The authors wish to acknowledge the enthusiastic co-operation of Mr. H. Williams (Development Engineering Group, D.E.R.E.) who designed and tested the Minerva equipment in the heat exchanger and made his results available, and of the Heat Exchange House staff who made the tests possible.

REFERENCES

- MEYER, A.S. and YOUNG, J.P. Detection of Traces of NaK in Air. ORNL 2340.
- FASSEL, V.A. and GOLIGHTLY, D.W. Detection Limits of Elements in the Spectra of Pre-mixed Oxy-acetylene Flames. Analyt. Chem., Vol.39, 1967, pp.466-476.

TABLE I

Reaction of Hot Sodium Escaping into Air

Sodium at 300°C Air at 160°C

Leak Rate	Reaction and Comments Sodium burns.		
Greater than 2g/min.			
About 0.5g/min.	Sodium sometimes burns or can form a melt of oxidation products which will fall off the leaking tube.		
Less than 0.1g/min.	Sodium doesn't burn and can form a melt of oxidation products which spread over the leaking tube. These products may or may not fall off the tube. If they do not fall off then a thick deposit of oxide or sodium carbonate will form eventually.		

TABLE II Detection of Hot Sodium Escaping into Air

Burning-Sodium Detectors Burning sodium releases Na ₂ O into air and light.	Air Sampling Detectors Need good air circulation in H.E. cubicle. Light Detectors		NH, compounds Atomic absorption detector Light absorption detectors
Non-Burning- Sodium Detectors Formation of melt of oxidation products.	Needs material to fall off the tube.	(viii)	Anodised aluminium wire grid*

^{** -} Examined in the laboratory and on the H.E. box.
* - Examined in the laboratory.

TABLE III

Comparison of Detectors

Detector	Sensitivity to Na or NaK	Needs Air Carrier?	Must Sodium Ignite?	Summary
Minerva	Detected 4g burning sodium in cubicle test.	Yes	Yes	Very easy to instrumentate and should not need much attention.
Flame Photometer	Detected 1g burning Na and 0.1g Na as carbonate spray in cubicle test.	Yes	Yes	Correction may have to be applied for background Na from sea spray. At some loss of sensitivity (down by 4) the K light could be used on those H.E. full of NaK and this would make the flame specific. Needs gas supply and naked flame but fairly easy to instrumentate.
pH, Conductivity	Not measured but calcula- tion shows ~1g.	Yes	Yes	Needs water supply, and some careful attention. Slow response, and difficult to automate.
NH ₃ Release	Not known but very poor.	Yes	Yes	Not reliable owing to thermal decomposition of ammonium compounds. Very difficult to instrumentate.
Atomic Absorption	Probably less sensitive than flame photometry.	Yes	Yes	Expensive and no advantages over flame photometry.
Light Absorption	Not known.	No	Yes	Detects smoke inside the cubicle. Should be easy to install and needs little attention.
Light Emission	Probably very sensitive.	No	Yes	Should detect occasional flashes of light. Fairly easy to install and needs little attention.
Al Grid	With 0.1" mesh 50 mg Na detected.	No	No	Reliable, easily instrumented, and detects all forms of leak. Fairly expensive to install, with work inside cubicles.

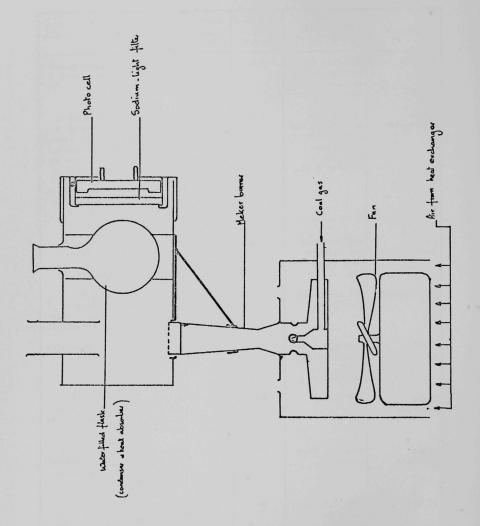
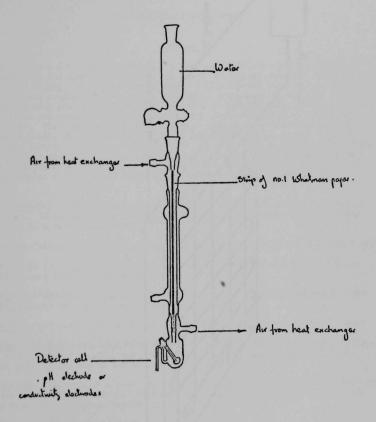
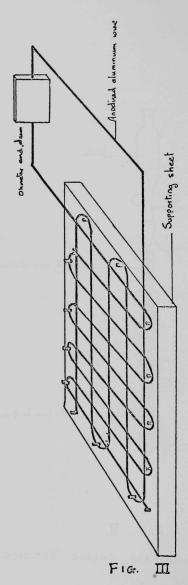


FIG. I FLAME PHOTOMETER DETECTOR



PH OR CONDUCTIVITY CHANGE DETECTOR



ALUMINIUM WIAR GRID DRIECTOR

3. Extinguishing Agents for Metal Fires

The material in this section was provided by Mr. M. R. Kraus, Manager, Product Services Department, The Ansul Company.

a. Ansul Extinguishing Agents for Combustible Metal Fires

ANSUL EXTINGUISHING AGENTS

FOR COMBUSTIBLE METAL FIRES

"MET-L-X"

"MET-L-X" is a dry powder composed of a salt base with additives to render it free-flowing and cause heat caking. It can be discharged through hose lines and fixed piping. Hand portable, wheeled, stationary and piped system extinguishers are available for use with "MET-L-X". They range in capacity from 30 pounds to 2000 pounds. The 30 pound hand and 150 and 350 pound wheeled models are listed and approved by Underwriters' Laboratories and Factory Natual Laboratories. The technique used to extinguish a metal fire with "MET-L-X" is to open the nozzle of the extinguisher fully and apply a thin layer of "MET-L-X" over the burning mass from a safe distance, until control is established. Then throttle the nozzle to produce a soft heavy stream and completely cover with a heavy layer from close range. The heat of the fire causes the "MET-L-X" to cake, forming a crust which excludes air and results in extinguishment.

MAGNESIUM--"MET-L-X" will completely extinguish dry or oily ohips, turnings or castings. It is especially suitable for casting fires because of its ability to cling to a vertical surface.

TITANIUM -- "MET-L-X" will control and in some cases extinguish small titanium fires.

WRANIUM-No tests have been conducted at Ansul. Field reports successful use on 12 or more fires at one location.

ZIRCONIUM-"MET-L-X" is suitable for the control and in some cases the complete extinguishment of fires in zirconium chips and turnings.

ALUMINUM--"MET-L-X" will completely extinguish small fires in aluminum powder.

SOBIUM-"MET-L-X" will completely extinguish sodium in depth and sodium spills. If, as a result of a spill, sodium adhered to a vertical surface, "MET-L-X" would cling to the sodium and extinguish the fire.

PCTASSIUM--If a perforated metal plate is placed just above or below the surface of the molten metal, "MET-L-X" will completely extinguish the fire. The plate aids crusted "MET-L-X" to bridge the fire area.

SCDIUM-POTASSIUM ALLOY (NAK) -- Same as potassium.

"LITH-X"

"LITH-X" is also a dry powder. It is composed of a special graphite base with additives to render it free-flowing so that it can be discharged from an extinguisher. "LITH-X" was developed meinly for use on lithium fires, but has proven to be very effective on other combustible metals. "LITH-X" is a standard Ansul product and is available in large or small quantities. The technique used to extinguish a metal fire with "LITH-X" is the same as the technique used with "MET-L-X". "LITH-X" does not cake or crust when applied over a burning metal. It excludes air and conducts heat away from the burning mass which results in extinguishment.

MAGRESING-"LITH-X" will completely extinguish dry or oily chips, turnings or castings. "LITH-X" will not cling to vertical surfaces so it will be necessary to completely cover a casting.

TITAMING-Although we have not tested "LITH-X" on titanium fires, we feel it should be effective for control and possibly complete extinguishment.

ZIRCONIUM--"LITH-X" is suitable for the control and in some cases the complete extinguishment of fires in zirconium chips and turnings.

SODIUM -- "LITH-X" will successfully extinguish sodium in depth and sodium spills.

SODIUM-POTASSIUM ALLOY (NAK) -- "LITH-X" will extinguish NAK spill fires and control fires in depth.

LITHIUM -- "LITH-X" will successfully extinguish lithium fires.

TRIMETHOXYBOROXINE

Trimethoxyboroxine (TMB) is a flammable liquid organometallic compound. It was produced by the Callery Chemical Company during their research on boron compounds. It was developed as an extinguishing agent by the Naval Research Laboratory for use on magnesium castings and structural shapes under aircraft crash fire conditions. TMB is applied from a $2\frac{1}{2}$ gallon stored pressure extinguisher which delivers either a spray or straight stream. The application of TMB on a metal fire results in a secondary Class B fire and large quantities of dense white fumes are liberated. As the organic matter in the material is burned away, a glassy boric oxide coating remains on the metal. This coating excludes air which results in extinguishment. TMB is only available in $2\frac{1}{2}$ gallon stored pressure extinguisher.

MAGNESIUM CASTINGS (Aircraft Crash Fire Fighting) -- The application of TMB on this type of fire will result in fast extinguishment which can be quickly followed by foam or water.

MAGNESIMA CHIPS, TURNINGS OR CASTINGS (Industrial Fires) -- TMB will completely extinguish fires in oily or dry chips, turnings or castings. If the fire occurs indoors, the heavy fuming of TMB may be undesirable.

TITANIUM -- TMB is suitable for control and in most cases the complete extinguishment of fire in titanium chips, turnings, sponge and powder.

ZIRCCNIUM -- TMB will control and in some cases completely extinguish fires in zirconium chips or turnings.

TMB is not recommended for fires in sodium, sodium-potassium alloy (NAK) and lithium. TMB reacts violently with lithium and NAK. Although TMB will extinguish sodium in depth, the protective coating formed by TMB picks up moisture very rapidly which in time may penetrate through to the sodium and result in a violent reaction.

Revised -- May 11, 1960

Recopied -- April 14, 1961

b. UL and FM Approval of "MET-L-X"

General Bulletin No. 735

June 24, 1958

FROM: Fire Equipment Sales Development Department

TO: All Distributors and Angul Offices

SURJECT: UL and FM Approval of "MET-L-X"

This will inform you that both the Underwriters' Laboratories and Factory Mutual Laboratories have tested and approved "MET-L-X" dry powder and our 30, 150 and 350 pound capacity "MET-L-X" extinguishers.

New extinguisher nameplates and new labels for "MET-L-X" pails are the only changes to the equipment and "MET-L-X" dry powder packages as result of this UL and FM testing. It appears it will still be sixty days before new nameplates will be received. Shortly thereafter you will be receiving "MET-L-X" extinguishers which have nameplates incorporating the Underwriters' label and Factory Mutual diamond.

In running approval tests, we determined certain limitations for "MET-L-X" extinguishers on various kinds of metal fires. This information should be helpful to you and your customers in determining fire protection requirements for metal hazards. The table below will give you a guide to extinguishing capacity for the various models based upon UL ratings.

Name of the Owner	"MET-	L-X" 30	"MET-	L-X" 150	"MET-	L-X" 350
HAZARD	AREA	QUANTITY OF METAL	AREA	QUANTITY OF METAL	AREA	QUANTITY OF METAL
Magnesium Chips		6 1b.		30 1ь.		72 lb.
Sodium Spill Depth:	5 sq. ft.	5 1b.	25 sq. ft.	25 lb.	60 sq. ft.	60. 1ъ.
Over 1/2 in.	3 sq. ft.	6 1b.	15 sq. ft.	30 lb.	36 sq. ft.	72 lb.
*Potassium Spill Depth:	5 sq. ft.	5 lb.	25 sq. ft.	25 lb.	60 sq. ft.	60 1ь.
Over 1/2 in.	3 oq. ft.	6 1b.	15 sq. ft.	30 1ь.	36 sq. ft.	72 lb.
*Sodium-Potassium Alloy Spill	3 sq. ft.	2 1b.	15 sq. ft.	10 1ь.	36 sq. ft.	24 lb.

*Extinguishing potassium or sodium-potassium alloys in depths over 1/2 in. requires the use of a grate located above or not more than 1/2 in. below the surface of the burning metal. The grate is comprised of a steel plate having about 35 per cent of the area opened by 3/8 in. holes spaced 9/16 in. on centers.

c. Demonstration of Ansul "MET-L-X" Extinguishers for Metal Fires

DEMONSTRATION OF ANSUL "MET-L-X" EXTINGUISHERS FOR METAL FIRES

Engineering Department Test Station Marinette, Wisconsin

The increasing use of magnesium, sodium and other highly reactive metals in research and industrial processes has spurred the development of an agent for the control and extinguishment of these fires. Although a compound desirable for use on burning magnesium had been developed and marketed during the recent war by Ansul Chemical Company, a search was begun for a dry powder effective on all types of metal fires. Last year, a preliminary showing of this new dry powder, Ansul "MET-L-X", was given. At that time, the material was used on both burning magnesium and sodium metals.

Throughout the past year, additional tests have been carried out. The dry powder has been tested for effectiveness on different metal fires, application techniques have been studied, and suitable extinguishing equipment has been designed for the safe, effective discharge of dry powder over the burning metal.

In the demonstration we attempted to pass on the experience gained from our test work. We showed the use of our equipment on magnesium, sodium, potassium, and sodium-potassium alloy fires. Both hand and wheeled extinguishers were used.

An Ansul "MET-L-X" Piped System was used to control and extinguish a sodium-potassium alloy fire by discharging "MET-L-X" Powder into an enclosed hazardous metal location. The use of such a system in an area where a metallic fire may be expected will either extinguish the fire or afford rapid control and reduction of the fire to a point that the area may be entered and portable extinguishers used to complete the extinguishment.

Although a great deal of knowledge was gained in the development work of the past year, it must be emphasized that work on the extinguishment of metal fires is still in the preliminary stage. In order to provide a background for the tests conducted and to report on the information obtained from the test program to the present time, the following comments were made prior to the demonstration.

"Before the demonstration of the use of "MET-L-X" dry powder on metal fires is started, we wish to explain the precautions having to do with safety during the running of the tests, and also to discuss in advance some of the factors involved in fire protection where metal fires are concerned.

"During the handling of liquid metals, it is possible that some of the metals will be spilled on the ground. If this happens, we will cover the spillage with "MET-L-X" dry powder and put a placard at that point to warn you to stay away from that area. As you entered the gate, you saw a sample of the type of placard to be used. Also, we are placing the residual metal in one location on the Test

Station which is roped off and placarded to warn you to stay out of that area. Should you wish to see the residual material after the "MET-L-X" dry powder has been applied and the test pans transferred to the disposal area, please check before going beyond the rope as there is a certain amount of hazard connected with close approach to the liquid metals.

"You will note that the Test Station crew involved in working on these test fires are thoroughly protected against flying burning metal. If you should wish to observe the burning metal or to observe the test pans after "MET-L-X" dry powder has been applied, we wish to limit the number of men from the audience in an exposed area at any one time to three and each of these three to be equipped with the face shields which we will provide. Some of you may think our precautions are excessive. However, we do not wish any of you to be injured nor do we wish any of our own personnel to be injured. The actual probability of a serious "blow" of burning liquid metal is small but we prefer to take full precautions.

"Please stay out of the fumes from the burning metal as they are strongly alkaline and can be harmful.

"MET-L-X" dry powder contains a small amount of material which partially decomposes, on being heated, to release some halogenated hydrocarbons. Although these are not released in large quantities, the fumes are noticeable in an enclosed location.

"We have been asked why we use sodium chloride as a base for "MET-L-X" dry powder instead of the sodium carbonate (soda ash) which is frequently used for sodium fires. The objections to the use of soda ash are:

- 1. There is no certainty that the soda ash will be anhydrous.
- 2. If soda ash contains over 3% water it will react with burning sodium.
- 3. Soda ash picks up moisture from the air to form a stable hydrate.
- Soda ash will react readily with burning metals such as magnesium, calcium, lithium, etc.
- Soda ash is alkaline and would be very objectionable when discharged around personnel.

"We wish to call to your attention that we consider this demonstration covers only the preliminary phases of fire protection for burning metals. We also wish to point out that where large quantities of liquid metals are concerned, the fire hazard and the difficulty of handling the materials increases with the temperature of the metal and the depth of the liquid metal. The use of "MET-L-X" dry powder as an extinguishing agent may be entirely satisfactory but special precautions must be taken with spills of large quantities of molten metals. For example, the sodium-potassium alloy is liquid at normal temperatures and has a specific gravity considerably less than that of "MET-L-X" dry powder. Accordingly, the "MET-L-X" dry powder tends to sink through the liquid metal which, being

continually exposed, continues to burn. To the best of our knowledge this problem exists with all metal-fire extinguishing agents.

"MET-L-X" dry powder 'cakes' under exposure to relatively high temperatures and will bridge liquid sodium at high temperatures in the 18 in. by 18 in. steel pans used in these tests. However, the bridging effect is not sufficiently strong for potassium or sodium-potassium alloys at high temperatures and in depth.

"We are using, and will show to you, a suggested method for handling this type of material where the spills are in depth. This method consists of covering the area which receives the spill with a perforated metal plate which will be above or just below the liquid metal level. The perforated metal plate which we are using in these tests has 3/8 in. holes on 9/16 in. centers in a plate 1/8 in. thick. Our tests have indicated that fires in low specific gravity liquid metals can be readily handled by using this arrangement.

"The average metal fire is likely to be relatively small and readily handled by the use of "MET-L-X" dry powder. We wish to emphasize that where large spills of liquid metals are concerned, the problem of fire protection involves much more than just the use of "MET-L-X" dry powder alone."

Some of the properties of flammable metals are:

Metal	Melting Point, OF.	Electromotive Series*	Boiling Point	20°C. Sp. Gr.
Sodium-Potassium Alloy	as low as 10	(No data)	Approx. 1400	0.775
Potassium	145	2. 9241	1400	0.87
Sodium	207	2.7146	1616	0.971
Lithium	367	2.9595	2460	0.534
Magnesium	1200	2.40	2030	1.74
Calcium	1490	2. 87	2190	1.55
Zirconium	3090	0.7618	Over 3800	6.4

^{*} Electromotive series as determined by potentials set up in water solutions referred to the hydrogen electrode as zero.

ANSUL "MET-L-X" EXTINGUISHERS FOR METAL FIRES

In our development and testing work on the extinguishment of fires in readily flammable metals, we have developed three models of Ansul "MET-L-X" dry powder extinguishers for metal fires, all of which are painted yellow to distinguish them from dry chemical fire extinguishers.

The Ansul "MET-L-X" 30 hand portable extinguisher is similar in appearance and principle of operation to the Ansul 30-B dry chemical extinguisher. The "MET-L-X" 30, however, differs somewhat in nozzle design in order to produce a stream of shorter range and lower velocity than the discharge from the Ansul 30-B dry chemical extinguisher. The low velocity of the "MET-L-X" stream is necessary to blanket the fire effectively and avoid agitating the burning metal.

Ansul "MET-L-X" Piped Systems, like Ansul Dry Chemical Piped Systems, permit the extinguishment of fires in locations where the hazard is too great for personnel to enter to extinguish the fire. Extinguishment of metal fires is accomplished with the Ansul "MET-L-X" Piped System by discharging "MET-L-X" dry powder through nozzles installed over the hazard area. The discharge coats all vertical surfaces and distributes an even layer of "MET-L-X" dry powder over the floor where most spilled liquid metal would collect. The Ansul "MET-L-X" Piped System unit is placed in a location separated from the liquid metal hazard area to avoid involvement in the metal fire and exposure to the metallic oxide fumes. This permits ready access by employees who also may safely actuate the piped system unit from a remote location.

The Ansul "MET-L-X 150 wheeled extinguisher may be used where equipment is required with greater capacity and versatility than a hand extinguisher. Like the Ansul Dry Chemical wheeled extinguishers, the "MET-L-X" 150 is equipped with a "Dualstream" nozzle. A high velocity "straight" stream is used where it is necessary to discharge the "MET-L-X" from a distance from the burning metal. The low velocity "fan" stream is used for close approach and the final effective covering of the metal.

SCHEDULED TESTS

Test Procedure

Test fires on magnesium castings and turnings were carried out by placing the magnesium in a pile on a steel plate, igniting the pile with an acetylene torch, and increasing the intensity of the fire by means of an oxygen jet. Extinguishment was begun when the fire had covered most of the surface area of the pile.

The more reactive metals were placed in 18 in. by 18 in. by 8 in. deep test pans and heated to the proper temperature over a propane burner. In most of the tests the highly reactive metals were heated to around 900°F. At that temperature the metals were in the liquid state with the entire surface area burning. The pan containing the burning metals was then removed from the burner and "MET-L-X" dry powder applied to the burning surface.

TESTS CONDUCTED WITH ANSUL "MET-L-X" 30 HAND EXTINGUISHER

Magnesium Turnings

Magnesium turnings, such as would be found in a shop machining magnesium castings, were piled on a steel plate. The pile was 18 in. in diameter and 12 in. high containing 11 1/2 lb. of magnesium. The flame from an acetylene torch was applied to the pile for 3 min. after which 90% of the exposed area was burning. The fire was then attacked with an Ansul "MET-L-X" 30 extinguisher and the fire intensity was greatly reduced in 10 sec. In 92 sec. the pile was completely covered with "MET-L-X" dry powder and in 2 min. 5 sec. the fire was extinguished. Because of the intense heat involved, the 30 lb. "MET-L-X" dry powder blanket partially decomposed and turned dark in spots 4 min. after the attack on the fire began, but the fire did not rekindle itself.

Magnesium Castings

Magnesium turnings were banked around a pile of magnesium castings to simulate a factory scrap pile. The weight of the pile was about 15 lb. and the scrap covered an area 22 in. indiameter with a height of 9 in. The pile was ignited and a jet of oxygen was applied to speed the ignition of the castings. The entire surface of the pile was burning and molten metal runs were observed after 9 min. The attack on the fire was made with an Ansul "MET-L-X" 30 extinguisher. Control of the fire was achieved in 4 sec. The pile was completely blanketed with "MET-L-X" dry powder in 56 sec. and the fire was extinguished in 2 min. 54 sec. Thirty pounds of "MET-L-X" powder were used to accomplish extinguishment.

Sodium (1/2 in. depth)

Sodium bars weighing a total of $7\ 1/2\ lb$, were melted in a $2\ 1/4\ sq$, ft. pan to a depth of about $1/2\ in$, and were further heated to $265\ F$, at which temperature the entire metal surface was burning. The preheat time was 8 min., 10 sec., and the sodium was allowed to burn for 1 min. 15 sec. before the attack with an Ansul "MET-L-X" 30 extinguisher. The fire was extinguished in 1 min. 2 sec. using the total contents of the "MET-L-X" 30.

Sodium (3 in. depth)

A more severe sodium fire was simulated by heating 36 lb. of sodium in a 2 1/4 sq. ft. steel pan. The molten sodium was brought to a temperature of 900^{0} F. in 17 min. 43 sec. After a 48 sec. preburn, a "MET-L-X" 30 extinguisher was pressurized and "MET-L-X" dry powder applied to the burning surface. The fire intensity was greatly reduced within 5 sec. and the fire completely extinguished in 61 sec. Again, the 30 lb. charge of the hand extinguisher was sufficient to extinguish the fire.

Potassium (1/2 in. depth)

A container of potassium metal was heated and 5 lb. of molten potassium was transferred to the 2 1/4 sq. ft. test pan under nitrogen pressure. The metal was heated for 4 min. 15 sec. to a temperature of 750° F. The fire was attacked

immediately and control was achieved in 8 sec. Extinguishment was completed in 26 sec. requiring the 30 lb. charge from the Ansul "MET-L-X" 30 hand extinguisher used on the fire.

Potassium (3 in. depth)

About 30 lb. of molten potassium was transferred to a test pan (2 1/4 sq. ft.). This gave a depth of metal of about 3 in. Because of the low specific gravity of the molten potassium, "MET-L-X" dry powder sinks through the metal allowing the burning to continue unhampered. To solve this problem, a perforated steel plate placed above the liquid metal surface was used to support the "MET-L-X" dry powder layer. The steel plate was made up of a 1 1/2 ft. square section of perforated 1/8 in. plate (3/8 in. holes on 9/16 in. centers) with four 1/2 in. by 1/2 in. angle iron legs, 4 in. long. The surface of the molten metal was about 1 in. below the perforated plate.

The molten mass was heated to 880°F, over a period of 12 min. 50 sec. When the potassium was up to temperature, it was allowed to burn for 20 sec. An Ansul "MET-L-X" 30 extinguisher was used to apply "MET-L-X" dry powder and the fire was extinguished in 56 sec. Thirty pounds of "MET-L-X" dry powder were used for the extinguishment.

A similar perforated steel plate might be used in actual practice to cover sumps or drainage troughs which would be used to collect spilled metals in areas where low density liquid metals were being handled in quantity. A layer of "MET-L-X" dry powder could then be built up over the perforated plate and the metal fires extinguished.

Sodium-Potassium Alloy (1/2 in. depth)

A test fire of sodium-potassium alloy 1/2 in. in depth was cancelled from the schedule of tests because of lack of time.

TEST CONDUCTED WITH ANSUL "MET-L-X" PIPED SYSTEM FOR METAL FIRES

An Ansul "MET-L-X" Piped System unit of 600 lb. capacity was connected to a four nozzle piped system installed in a metal enclosure 7 ft. long by 6 ft. wide by 7 ft. high. Thirty-five pounds of liquid sodium-potassium alloy were transferred to a 2 1/4 sq. ft. test pan, covered with a perforated steel plate, and heated to 900°F., the preheat period being 14 min. 45 sec. The pan was carried into the enclosure and allowed a preburn period of 2 min. 1 sec. The "MET-L-X" Piped System was then actuated manually and "MET-L-X" dry powder was discharged for 2 min. 15 sec. Because of the high rate of "MET-L-X" dry powder application, the extinguishment time was estimated at 30 sec.

After the discharge of the system was complete, the test pan was observed to have about a 4 in. depth of "MET-L-X" dry powder above the perforated steel plate. This layer of "MET-L-X" dry powder above the metal was considerably thicker than the "MET-L-X" dry powder layer necessary to extinguish previous fires with the use of Ansul "MET-L-X" dry powder hand extinguisher. As a piped

system is laid out to extinguish the most severe fire in any portion of the protected area, more dry powder is provided than would normally be needed when the dry powder can be applied manually to just those burning portions of metal.

TESTS CONDUCTED WITH ANSUL "MET-L-X" 150 WHEELED EXTINGUISHERS

Magnesium Turnings

Twenty-nine pounds of magnesium turnings were piled on a steel plate covering an area 30 in. in diameter and 15 in. high. The acetylene torch and oxygen jet were applied to the pile for a period of 22 min. 55 sec. After this preheat the entire surface area was burning, and the fire was attacked with an Ansul "MET-L-X" 150 wheeled extinguisher. The attack was made with the "fan" stream of the "Dualstream" nozzle at close range. The fire was unusually severe but the fire intensity was reduced drastically in 10 sec. of "MET-L-X" dry powder application. The burning area was completely covered with "MET-L-X" dry powder in 45 sec. and extinguishment was accomplished in 1 min. 50 sec. About 100 lb. of "MET-L-X" dry powder was used.

Magnesium Castings

Magnesium castings were piled on a steel plate and magnesium turnings banked around the castings. The pile, made up of 35 lbs, of magnesium, was 10 in. high and 30 in. in diameter. Ignition was made with the oxy-acetylene flame and burning was intensified by the application of oxygen. After 11 min. 50 sec., 85% of the surface area was burning. The attack was then made with an Ansul "MET-L-X" 150 wheeled extinguisher and the "fan" stream of the "Dualstream" nozzle employed for close approach to the burning pile. The fire was well under control in 8 sec. Forty seconds after the beginning of the attack, the entire pile was blanketed with "MET-L-X" dry powder and after 1 min. 50 sec. the fire was extinguished using a total of 100 lbs. of "MET-L-X" dry powder.

UNSCHEDULED TESTS

Additional fire tests were run on samples of metals furnished by some of the organizations represented at the tests.

Lithium

Seven and one-half pounds of lithium were melted in a 2 1/4 sq. ft. test pan giving a depth of about 1 1/4 in. The metal was heated to a temperature of 900^{0} F. during a preheat period of 21 min. 5 sec. after which the pan was moved into the test house. The moving operation allowed the lithium a preburn period of 1 min. 40 sec.

The fire was attacked with an Ansul "MET-L-X" 30 extinguisher and the entire contents of the extinguisher were expelled over the burning area. The "MET-L-X" dry powder sank through the molten lithium and the fire continued unabated. The contents of a second Ansul "MET-L-X" 30 applied to the burning

metal covered the pan area and extinguished the fire momentarily. However, soon after extinguishment, the entire "MET-L-X" dry powder mass sank through the liquid metal and the hot lithium began to burn again. A perforated steel plate was then placed in the pan and the contents of a third "MET-L-X" 30 distributed over the perforated plate. Control of the fire was gained 30 sec. after the initiation of the third attack and extinguishment was complete with the expulsion of all the "MET-L-X" dry powder in the extinguisher. A total of about 90 lbs. of "MET-L-X" dry powder was used. Later examination of the cooled mass disclosed large quantities of unburned metal.

Calcium

Five pounds of granulated calcium were placed in a $2\ 1/4$ sq. ft. test pan and heated with the propane flame and acetylene torch for $12\ \text{min}$. $40\ \text{sec}$. Unlike the low melting point metals, the calcium burned without melting. Because of the small amount of calcium tested, the pile burned itself out before extinguishment could be attempted. It was concluded that a minimum of $30\ \text{lb}$. of calcium would be required for a practical test.

Zirconium

A very small amount of zirconium turnings (about 3 oz. to 4 oz.) was lighted with a match and when the mass was glowing throughout, "MET-L-X" dry powder was applied from a hand extinguisher and the fire extinguished in 6 sec.

"Silex"

An estimated 4 lb. of briquettes of mixture designated as "Silex" was tested next. The mixture is similar to "thermite" in that it supplies its own oxygen, the active components of the mixture being silicon and sodium nitrate. Ignition was accomplished by applying an oxy-acetylene flame to the cardboard carton in which the "Silex" was supplied. After 3 min. of flame application, the briquettes were allowed to burn for 1 min. 10 sec. before extinguishment was attempted with an Ansul "MET-L-X" 30. The burning mass was covered with "MET-L-X" dry powder in 2 min., but because the "Silex" contained its own oxygen, flames eventually broke through the "MET-L-X" dry powder layer and burning continued.

Granulated Magnesium

The final test of the demonstration was conducted on granulated magnesium. The fire was set up in the 7 ft. by 6 ft. by 7 ft. enclosure supplied by the Ansul "MET-L-X" Piped System unit (600 lb. capacity) through four discharge nozzles. In the enclosure was a large steel pan in which there was a closed halfdrum containing 40 lbs. of granules, an open can filled with 20 lbs. of magnesium granules, and 10 lb. of the granules spilled on the pan bottom adjacent to the open can. The granules were about 1/16 in. in diameter. The acetylene torch was applied to the spilled material for 35 sec. and the fire allowed to spread for 4 min. 5 sec. After the preburn, 65% of the surface of the floor pile was burning, but there was no evidence of fire in the can or half drum. The enclosure was then closed and the "MET-L-X" piped system actuated. The duration of the discharge was 2 min.

14 sec., and it was estimated that the fire was extinguished in 30 sec. When the enclosure was opened after discharge, the half-drum, can and floor pile were heavily coated with "MET-L-X" dry powder indicating very fast extinguishment.

CONCL USIONS

Because of the qualitative nature of the preliminary tests carried out on metal fires on August 2, 1950, it is considered that the test fires established only that metal fires can be extinguished under the conditions of the tests. It is also considered that the demonstration indicated rather conclusively that fire protection for large quantities of flammable liquid metals involves other factors than just the use of a suitable extinguishing agent.

In addition, it is thought that the tests indicated the desirability of the use of perforated plates and a subdivided collection area in locations where large spills of liquid metal may be possible.

Each condition of use of the reactive metal considered in this report presents a special fire protection problem. We are firmly convinced that much remains to be done in testing, development, and study of the basic fire protection problems incidental to the handling of these readily flammable metals. Particularly, it is emphasized that quantitative studies should be considered at this time.

No. 4455

Copied 3/21/62

APPENDIX C

Liquid-metal Fires and Scrubber Systems

 Letter to F. A. Smith from O. G. Jenkins, Jr., and J. J. Droher (69LMEC-686), General Information and List of Films on Liquid-metal Fires and of Reported Accidental Sodium Fires



Liquid Metal Engineering Center



Operated for the U.S. Atomic Energy Commission by Atomics International

June 4, 1969

In reply refer 69LMEC-686

Mr. Fred A. Smith Argonne National Laboratory Reactor Engineering Building 308 9700 South Cass Avenue Argonne, Illinois 60439

Dear Fred:

We are pleased to respond to your request for available information pertaining to sodium (liquid metal) fires with a particular interest in: information related to the nature of sodium fires, scrubbing equipment used at HNPF, a tabular list of known or reported sodium fires, and a list of liquid-metal fire fighting film. Enclosed are 119 computer printouts containing bibliographic information and abstracts of documents dealing with all aspects of sodium and NaK reactions with air. The documents listed in these printouts contain information concerning: (1) accidental sodium fires, (2) scrubbers and other devices for treatment of aerosol releases from alkali metal fires, (3) sodium burning experiments conducted to determine energy-release rates, fission-product and aerosol release rates, (4) alkalimetal fire suppression methods, and (5) precautions taken against the occurrence of sodium fires.

Please note that in some cases the computer printouts include the notation of "Limited Distribution"; this notation indicates that the referenced document has some type of marking or stamping which precludes distribution to the general public and limits its release to a specified group (e.g., AEC and AEC contractors only). The specific distribution limitations on any such report (which is usually given in our abstract) should be honored if you use material from reports or quote them as references.

Also enclosed is a copy of a summary of information on sodium fires and on sodium or plutonium aerosols as they pertain to sodium fires, which was compiled by Mr. D. E. Lew (another member of the LMIC staff) in answer to a recent inquiry. This summary contains very

pertinent information related to pool fires, spray and explosive ejection fires, generation of sodium and/or plutonium aerosols during sodium burning, and computer codes related to sodium fires.

A scan of the computer printouts for publications containing guidance on preventing and safely suppressing sodium fires revealed the following list of particularly pertinent documents:

- (LM-00641) A. Thorley and A. C. Raine, "Guidance in the Safe Handling of Alkali Metals," UKAEA TRG Report 25(C)
- (LM-02178) M. Sittig, "Safe Handling of Alkali Metals," IECH-48-227-56
- 3. (LM-02091) D. Nelson et al., "Guide to Liquid Metal Handling," AECU-1273
- (LM-03593) S. J. Rodgers and W. A. Everson, "Extinguishment of Alkali Metal Fires. Quarterly Progress Report No. 3, September 15 to December 16, 1962," MSAR-63-19
- 5. (LM-00898) J. D. Gracie and J. J. Droher, "A Study of Sodium Fires," NAA-SR-4383
- 6. (LM-05089) F. A. Anderson, "A Primer for the Safe Use of Liquid Alkali Metals," ORNL-TM-1740
- 7. (LM-04652) P. L. Hill, "Alkali Metals Area Safety Guide," (Supplemental Issue) Y-811

In addition to the foregoing list of references, other good sources of guidance are publications issued by companies who manufacture sodium, namely: E. I. Du Pont de Nemours and Co., Ethyl Corporation, and National Distillers Chemical Company.

Regarding your request for information pertaining to the HNPF Dry Scrubber System, the enclosed portion of Supplement 4 to NAA-SR-5700 contains a schematic diagram of the system and a rather comprehensive description of the system and its mode of operation. Also included are discussions of preliminary bench-scale tests conducted on the filter medium using sodium smoke from a test generator and final tests conducted on a model glass-fiber, bag-type filter of the type installed at Hallam. In the final tests on the model the efficiency of the filter assembly for the removal of alkali metal combustion products was demonstrated along with the ability to efficiently clean and recoat the filter bags using the methods which were planned for use on the actual HNPF Dry Scrubber System.

The sodium oxide scrubber was a late addition to the heating and ventilating system, and was purchased as package unit addition. After installation much work was required to make the system operable. The many air-operated valves in the system were a source of difficulty, in that dirty air-lines fouled actuating solenoids and piston operators. This problem was eased by adding supply air-lines strainers and blowing out some of the air supply lines, and it disappeared as the system cleaned itself.

Another problem area was the reclaim cycle. The conveyor system was designed to handle the flow from the two feeders under the hoppers and return the asbestos to the storage unit. The system required redesign at both terminals. At the feeder end, slots had to be cut in the waste storage pit barricade gates to get supply air to the pneumatic conveyor. The entrance from the duct to the conveyor system had to be enlarged to prevent plugging. At the discharge end of the reclaim system the asbestos was collected in bags at the top of the storage silo and dumped into storage. Since the bags were not emptying satisfactorily, a bag cleaning system had to be installed.

Due to poor grading around the waste storage a problem of ground water collection in the waste storage pit existed. This problem was solved by pouring a concrete slab around the storage pit and grading the surrounding area to provide proper runoff of surface water.

The next item that you requested was a listing of known or reported sodium fires which occurred accidently (i. e., were not deliberately initiated to study either the nature of sodium fires or methods of extinguishing sodium fires). Published documents in our data bank were examined and references were found to four accidental sodium fires; members of our technical staff were aware of two other accidental sodium fires. The enclosed tabular listing gives the location, time of occurrence, cause, damage, and information source for these six accidental fires. Undoubtedly, a number of other accidental sodium fires have occurred which have not been documented in any formal manner. Under a Maintenance and Malfunction Analysis Program, the Liquid Metal Engineering Center is collecting data on malfunctions and incidents or unusual occurrences. It is possible that other accidental sodium fires, not otherwise documented, will be unearthed by this effort.

The final topic about which you requested information was a listing of films on combating liquid-metal fires. The 1968 guide to AEC Safety Films (Exchange Program) prepared by the Division of Operational Safety, United States Atomic Energy Commission was searched for films on liquid-metal fire fighting. One of the listed films, "Alkali Metals Reactions and Fire Control," appears to be ideally suited for application to your problem. This is a thirty-minute, color film which describes the burning characteristics of alkali metals and methods of fire control with various extinguishing agents. It also shows disposal procedures for contaminated alkali

metals. This film is available for loan, on two to four weeks advance notice, from any of the following sources:

- Safety Branch
 U.S. Atomic Energy Commission
 Oak Ridge Operations Office
 P.O. Box E
 Oak Ridge, Tennessee 37831
- Union Carbide Corporation, Nuclear Division Oak Ridge National Laboratory P.O. Box X Oak Ridge, Tennessee 37831
- Director of Information
 U.S. Atomic Energy Commission
 Idaho Operations Office
 P.O. Box 2108
 Idaho Falls, Idaho 83401

The USAEC Film Catalog (Professional Level) was also searched for films on liquid-metal fire fighting. In this listing there was a 14-minute film entitled, "Fire Fighting in the Nuclear Age," which was produced for the USAEC by the Office of Information, Idaho Operations Office, USAEC. This film covers the use of protective clothing, respiratory protection, and special precautions taken while extinguishing burning radioactive materials. Some of the material in this film may be similar to that which would be included in a film on liquid-metal fire fighting. This film is available for loan, without charge, from USAEC headquarters and field libraries. The address of the field library nearest you is:

Ruth Jones *
Information Office
U. S. Atomic Energy Commission
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois 60439
Telephone: 312-739-7711, Ext. 2109

Also enclosed is a copy of a description of another film, "Sodium Expulsion into Air," from the Argonne National Laboratory, May 1969 Catalog of New Motion Picture Films, which may have some application to sodium fire fighting.

We recall viewing an ORNL film about 15 or 20 years ago which dealt with sodium disposal and with liquid-metal fires. Although we have not been able to find any published reference to this film, personnel at ORNL should be able to track it down if you are interested. We also are aware of some

^{*}Editor's Note: Ruth Jones at the Chicago Operations Office supplies films to requesters from Illinois, Indiana, Iowa, Michigan, Minnesota, Missouri, North Dakota, Ohio, South Dakota, and Wisconsin.

ANL

Mr. Fred A. Smith

-5-

June 4, 1969 69LMEC-686

"raw footage" film at Atomics International made during "planned" sodiumfires experiments. It is quite possible that similar footage is on hand at other sites performing work involving sodium, and perhaps even by the major suppliers of sodium or NaK. We are attempting to accumulate this type of information as the opportunity arises, but we trust that you can appreciate the difficulty involved in locating material which has not been published or released.

It was a pleasure to serve you again, Fred. Should the efforts of your ad hoc group on sodium fires result in any publications, formal or informal, which are available to the Commission or its contractors, would you send a copy to the Liquid Metals Information Center. Kindly notify us before forwarding if there is a charge involved. Your cooperation in this matter will help us in providing the best service possible to our users.

Best regards,

O. G. Jenkins, Jr.

Liquid Metals Information Center

y y Dnohen

J. J. Droher, Supervisor Liquid Metals Information Center

Enclosures

TABULAR LISTING OF KNOWN AND REPORTED ACCIDENTAL SODIUM FIRES

IADULAN	C LIBITIO OF THE		
Location and App. Time	Cause	Damage Incurred	Information Source
Alplaus (WMAR) Atmospheric Sodium Pressure Still November 3, 1949 and December 23, 1949	First fire due to failure of brass fitting on inlet argon supply line to stainless steel still. Copper line and brass fitting replaced by welded steel pipe; second fire due to faulty weld where stainless steel gas line connected to still pot.	Some corrosion of stainless- steel shell due to contact with sodium combustion products. Heating oven fire brick had to be re- placed when contaminated with sodium oxide.	E. E. Baldwin, "Investigation of Alplaus Atmospheric Pressure Sodium Still," KAPL-337 (July 6, 1950)
Primary Gallery of SRE (sometime in 1958)	Electrical heater shorted and the resulting arc created a hole in 2-in. pipe leading from sodium service vault to primary heat transfer line. Plugs had been removed for other maintenance effort and gallery was exposed to air atmosphere when leak occurred.	Heat and combustion products damaged some heater and instrument lead wires which had to be replaced. Extensive survey of surroundings revealed no evidence of any fission product release from burning primary sodium. (Primary sodium known to contain some fission products.)	Discussion with operations personnel.
Atomics International Sodium Laboratory August 16, 1959	Tetralin used for cooling tank of sodium in a natural-convection heat-transfer experiment exploded, rupturing sodium tank and releasing sodium into air atmosphere in laboratory. Sodium was scattered throughout the building causing numerous small	Damage mostly due to tetralin explosion. Damage from sodium fires, while widespread, was mostly superficial. Large pool of burning sodium at bottom of experiment extinguished with negligible damage.	J. S. McDonald, J. E. Owens, "Investigation of Tetralin Explosion," NAA-SR-4803 (March 1, 1960)

fires.

TABULAR LISTING OF KNOWN AND REPORTED ACCIDENTAL SODIUM FIRES (cont)

Location and App. Time	Cause	Damage Incurred	Information Source
HNPF IHX Cell December 4, 1962	Residual sodium from damaged IHX was being drained into barrel through temporary drain line heated with propane torch. More sodium was drained than anticipated and calcium carbonate layer formed insufficient thermal barrier. Burning sodium penetrated bottom of barrel and ignited wooden support scaffolding.	Fire extinguished by operations crew before any appreciable damage occurred.	Discussions with operations personnel.
HNPF Carbon Trap Cell December 26, 1962	Line was opened for removal of sampler from carbon trap while carbon trap pressurized to about 6 psig. The sodium "heel" in the carbon trap was still molten and sprayed out into the surrounding cell.	Some minor damage to electrical and thermocouple leads. Deterioration of thermal insulation around carbon trap and piping. Aluminum jacketing melted.	ORNL-NSIC-17, "Abnormal Reactor Operating Expe- riences"(August 1966)
EBR-II West Wing Operations Room Sodium Boiler Plant February 9, 1968	Freeze plug formed in pip- ing to permit maintenance of bellows seal valve; due to insufficient cooling the freeze plug melted and al- lowed sodium to flow from open valve bonnet. Sodium ignited.	Damage superficial.	Argonne National Laboratory, Idaho Division, "Report of EBR-II Operations — January 1, 1968 thru March 31, 1968"

Attachment: 69LMEC-686

LEGAL NOTICE

This report was prepared under the sponsorship of the United States Atomic Energy Commission. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission' includes any employee or contractor of the United States Atomic Energy Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Liquid Metals Information Center

2. Film: Sodium Expulsion into Air

ANL-MP-730-111, color, silent, 5-1/2 minutes

Silent, high-speed film sequences of sodium-air reactions were taken as part of laboratory-scale experiments to study the effect of the geometry of building enclosures on the pressure buildup with time. Each run is labeled as to the weight of sodium, temperature and pressure, plus the height and diameter of the enclosures. Primarily for specialists. 1966

3. Summary of Information on Sodium Fires and on Sodium or Plutonium
Aerosols as They Pertain to Sodium Fires

Enclosure to 69LMEC-398
To: Mr. J. A. Zoubek
Westinghouse Electric Corporation

SUMMARY OF INFORMATION
ON
SODIUM FIRES AND ON
SODIUM OR PLUTONIUM AEROSOLS
AS THEY PERTAIN TO SODIUM FIRES

Compiled by: D. E. Lew Liquid Metals Information Center April 1, 1969

SUMMARY OF INFORMATION ON SODIUM FIRES AND ON SODIUM OR PLUTONIUM AEROSOLS AS THEY PERTAIN TO SODIUM FIRES

An excellent document covering work done in the field of sodium burning and aerosol release is R. E. MacPherson's, "Sodium Burning and Aerosol Release--An Evaluation of the State-of-the-Art" (Reference 1). In addition to a bibliography of 26 publications, it contains discussions, conclusions drawn from experimental studies, and recommendations for further work in pool burning, spray and explosive injection burning, and aerosol production, transport, and control. It states,

"Sodium fires can be subdivided into those fires characterized by combustion of a sodium pool and those due to a leak or rupture that produces a burning spray. A special case of the spray fire is one in which sodium is introduced explosively into an oxidizing atmosphere.

"Pool fires normally result from the accumulation of sodium on flat or recessed surfaces following either the rupture of sodium-containing equipment or the development of spray-producing leaks. The pool fire is characterized by a slower burning rate than that of a spray fire because of limited access of oxygen to the reaction zone. The rate of energy release is normally low, and extremes of temperature and pressure do not develop in an enclosed volume containing such a fire.

"The spray fire has all the problems associated with the pool fire; However, the problems are compounded by the increased reaction rate that results from more intimate contact between the sodium and air. The rate of energy release in a spray fire is a function of the reactant temperatures, the spray energy or degree of dispersion, the humidity, the oxygen concentration, and the geometry of the gas volume. The specific case of a spray fire that involves the explosive introduction of sodium into a surrounding atmosphere is of particular concern because the extremes of temperature and pressure would be expected in this case."

A second general reference, Chapter 19 of the revised version of the Sodium-NaK Engineering Handbook, will have an extensive coverage of liquid metal-air reactions. Included will be pool and spray fires, the influence of oxygen and moisture contents on burning, the physics of sodium fire aerosols, air cleaning requirements for sodium fires, and methods of fire fighting.

A section of Chapter 10, Safety, of the LMFBR Program Plan (Reference 2), also deals with sodium fires. The "background information" in this chapter should be of interest as well as the references cited.

A large share of the work in sodium pool and spray burning has been conducted by Atomics International. A review of experimentation to 1960 is included in Reference 3. This document describes the combustion process as well as discussing burning rates and ignition temperatures, the latter being a property dependent on such variables as the surface-mass ratio, surface conditions, metal purity, absolute humidity, temperature of the surrounding atmosphere, and air velocity over the surface. Fine particles of sodium condensed from a vapor mist may ignite at room temperature; droplets of sodium sprayed into air may not ignite until 250°F; a pool will not ignite until above about 400°F if the surface is disturbed to remove the oxide scum, and above 550°F if the surface is undisturbed. In some cases, undisturbed sodium has been heated to above 800°F before there was any evidence of ignition.

POOL FIRES

Sodium pool fire tests to determine rate of combustion have been conducted at various installations; a summary of the results is given in the attached table.

In a majority of the experiments systematic parameter variation was not attempted, techniques for estimating burning rates were limited, and detailed temperature measurements were not obtained. For these reasons the table shows combustion rates varying from 1 to 17 lb/hr-ft². The suggested range of values for sodium pool burning in air is 5-10 lb/hr-ft² based on results of References 4 and 16 where experiments were conducted in insulated containers with exposed sodium areas greater than 1 ft². In these two cases, the pool surface temperature rose to about 1200-1300°F, though initial sodium temperatures varied by as much as 500°F.

Data on the burning rate of sodium pools in reduced oxygen atmospheres (a technique used in reactor enclosures to reduce the consequences of sodium leaks and spills) is of interest, as energy and smoke can be liberated but at reduced rates. Work at Atomics International (Reference 3) demonstrated that at oxygen concentrations of 4 vol % and below, sodium at 1000° F did not undergo rapid combustion, but a slow reaction occurred at concentrations down to 0.1 vol %. Pool burning rates of sodium at 1000° F at oxygen concentrations from 1 to 4 vol % (nitrogen diluent) under forced flow conditions (Reference 5) indicate that the combustion rate is proportional to oxygen concentration, neglecting gas flow rate variations, with a value of 0.4 lb/hr-ft^2 -% O_2 . Extrapolation to air conditions gives a rate of 8 lb/hr-ft^2 , in good agreement with References 4 and 16, noted above.

The Large Fire Test No. 1 (LF-1) apparatus and initial test results are presented in Reference 4. The large-fires chamber can accommodate 5-ft diameter by 5-ft high pots, although the pot used in the experiment

cited was only 2 feet in diameter. Measurements of sodium burning, sodium oxide, and iodine release rates with time were accomplished quite readily. An overall average burning rate of 6.2 lb/hr-ft² was obtained in addition to fallout and deposition results.

Analyses of experimental results are applied to the Fast Reactor Core Test Facility (FRCTF) in Reference 9. Results are presented on liquid sodium energy release rates, sodium vapor and oxide release rates, iodine release rates, and particle-size distributions. Cases of "stirred" settling and no mixing or "tranquil" particle settling are considered.

AI experiments were also conducted in a laboratory test chamber to study the behavior of oxidized sodium released from a sodium pool fire. The test chamber was 40 ft³ in volume (3 feet in diameter by 7 feet high) with a total surface area of 108 ft² and a floor area of 6.75 ft². In all experiments, measurements were made of: (1) the airborne concentration and particle size distribution vs time, (2) the mass and activity deposition rate on the floor and walls, (3) the total amount of activity and mass deposited on the walls and floor, and (4) the initial and remaining quantity of mass in the burn pot. Results of six experiments are given in References 10 (Tests 1-4), 11 (Tests 4-6), 12 (Tests 1-5), and 13.

Presented at a recent conference was a paper covering both sodium pool fire and sodium spray-air reaction studies at AI (Reference 14).

Work at AI in the field of sodium fires, both pool and spray types, is summarized in quarterly and annual progress reports (Reference 15).

Detailed laboratory-scale studies by Longton (References 17 and 18) indicate that the humidity as well as the oxygen content should be specified. He investigated the reaction of distilled sodium with respect to oxygen pressure, gas moisture content, and temperature. The specific type of reactivity displayed was critically dependent on the partial pressure of water vapor present, and, to a lesser extent, on the oxygen partial pressure. Hydrogen influences the reaction of sodium and oxygen in a manner directly comparable to that of water vapor.

SPRAY AND EXPLOSIVE EJECTION FIRES

A comparison of a theoretical analysis of sodium-air reactions with two experimental studies is given in Reference 19. The theoretical problem was described by a system of seven differential equations and was evaluated on an analogue computer. The results were compared to the work of Hines, Gemant, and Kelley (Reference 20) in which sodium was injected continuously for 20 seconds into a closed steel container and to the work of Humphreys (Reference 21) where the sodium was injected in one single impact into the test chamber.

Humphreys' equipment at Argonne National Laboratory permitted the explosive injection of 400°C sodium into a 3-ft diameter, 10-ft high air-filled reaction vessel. The effects on vessel pressure and temperature of variations in sodium-oxygen molar ratios, initial sodium particle size, sodium dispersion within the vessel, and water vapor were studied. The test results are given in tabular form in References 21 and 22, and are considered with respect to the large containment system of EBR II.

Another ANL study involved a technique to study the expulsion of molten sodium into air (Reference 23). Preliminary experiments were carried out with the ejection of both water and sodium into air. The results and comparison of the two ejections are presented. The need for this work was related to the FARET containment design.

Also related to FARET was a 1963 Al evaluation of pressure increase in the hot cell from a sodium fire and in the primary vault from a hot sodium spill. The study is reported on in Reference 24.

References 3 and 25 discuss the influence of oxygen on spray burning. Gracie and Droher (Reference 3) state that the rate of pressure rise increased as the oxygen concentration increased (0 to 5 volume %), as the sodium temperature increased (600 to $1200^{\circ}F$), and as the gas moisture content increased (3 to 300 grains/lb of gas).

Experimental work underway at AI involves a study of the characteristics of high concentration sprays of liquid sodium in reduced oxygen atmospheres and in air (Reference 26). The concentration and particle size distribution of the material remaining in the air after the spray injection and reaction period are measured.

French study is concerned with the consequences of a sudden primary circuit rupture which could release sodium contaminated by fission products into the atmosphere. As an initial step in this investigation, liquid sodium containing iodine at 1100°C was explosively injected into a closed chamber filled with air. The experimental results and conclusions are reported in Reference 27 with more recent work described in Reference 28.

In addition to the development of fire fighting materials, Reference 29 reports on a preliminary investigation of the effect of burning sodium in contact with concrete.

SODIUM AND/OR PLUTONIUM AEROSOLS

A theoretical treatment of aerosol particle agglomerations and deposition is covered in References 30-32. A digital computer was used in solving the equation that describes in time the behavior of an aerosol.

A sodium aerosol generator built to produce aerosols useful in evaluating sizing devices is described in Reference 33. The generator can produce particulates similar to those created initially in a sodium fire and can be utilized for obtaining information on sodium aerosol characteristics.

Work by Ettinger, Moss, and Busey (References 34-36) resulted in determination of size characteristics of the aerosol produced during sodium and plutonium fires in atmospheres of various oxygen-nitrogen mixtures. Small-scale (grams of sodium) and large-scale (600 pounds of sodium) sodium fires produced aerosols with comparable size characteristics. Data also were obtained for plutonium fires and for fires involving both reactor fuel and coolant. References are given in Reference 36 for other investigations of aerosol characteristics of airborne plutonium produced from fires.

COMPUTER CODES

While discussing work at Atomics International previously, the use of a digital computer to study sodium aerosol behavior was noted (References 30-32). A telephone conversation with Mr. Melvin Silberberg of AI revealed that two computer codes for sodium fire analysis are also being used there, and one code is in the developmental stage. The AI code SOFIRE-1 deals solely with pool fires. A second code, originated at Argonne by programmer J. Anderson, is concerned theoretically with the case of an explosive spray fire. Its title is "Chemical Equilibrium Calculations" and its designation, ANL Program B-194 (3600°F). The AI code originally designated TRANSBURN and now referred to as SOFIRE-2 is being developed and, as yet, is not ready for accident calculations.

SODIUM POOL BURNING IN AIR

Container Area (ft ²)	Air Circulation	Container Depth (in.)	Original Sodium Weight (Ib)	Initial Sodium Temperature (^O F)	Burning Time (hr)	Burning Rate (lb/hr-ft2)*
1.67(3)	Natural	2	14	5	0.75	11
0.83(3)	Natural	2	7	9	0.75	11
0.14(3)	Natural	2	1	9	0.50	17
6.25(16)	Natural	3	50	850	1.6	6.3
6.25(16)	Forced	3	50	675	1.6	4.9
-(37)	Natural	-	-	930	-	3.6
2.78(38)	Natural	20	350	750	17	2.3
2.78(38)	Natural	22	400	750	10	2.1
2.78(38)	Natural	14	300	750	12	1.1
20.0(38)	Natural	17	320	750	18	1.1
20.0(15)	Natural	40	3500	500	26	1.5
0.6(4)	Natural	18	33	800	5.5	4
0.6(4)	Forced	36	83	800	11	5.5
3.1 ⁽⁴⁾	Forced	48	615	350	33	6.0 (9.0 max [†])

^{*}Average burning rate based upon time required for complete combustion of sodium or estimated fraction which burned, except in last test which was accurate determination by oxygen analysis.

Maximum burning rate reached after 1 hour.

Not reported.

Numbers in parentheses refer to references.

REFERENCES

- 1. R. E. MacPherson, "Sodium Burning and Aerosol Release--An Evaluation of the State-of-the-Art," ORNL-TM-1937 (May 6, 1968)
- "Liquid Metal Fast Breeder Reactor Program Plan, Volume 10, Safety," WASH-1110 (August 1968)
- J. D. Gracie and J. J. Droher, "A Study of Sodium Fires," NAA-SR-4383 (October 15, 1960)
- 4. G. N. Lauben, "Initial Experience with Large Sodium Fires Experiments (LF-1)," NAA-SR-12041 (August 1, 1966)
- G. N. Lauben and C. L. Larson, "Characterization of Source Terms for Aerosol Transport During Sodium Fires," Proceedings of the Ninth AEC Air Cleaning Conference, Boston, September 13-16, 1966, CONF-660904, 28
- A. A. Jarrett, G. N. Lauben, and R. L. Koontz, "Sodium Fires and the Release Characteristics of Particulates and Fission Products," International Symposium on Fission Product Release and Transport Under Accident Conditions, Oak Ridge, April 5-7, 1965, CONF-650407, 94
- G. N. Lauben et al., "Sodium Fires and the Release Characteristics of Particulates and Fission Products," NAA-SR-MEMO-9719 (April 5, 1965)
- P. A. Lottes, "Toward an Understanding of Sodium Fires," Power Reactor Technology and Reactor Fuel Processing 10, No. 1, 17
- 9. G. N. Lauben et al., "Study of Sodium Fires and Particulate Release as Applied to the FRCTF," NAA-SR-MEMO-11403 (June 1966)
- C. T. Nelson, L. Baurmash, and R. L. Koontz, "Techniques for Sampling Sodium Smoke and Fission Products," Proceedings of the Ninth AEC Air Cleaning Conference, Boston, September 13-16, 1966, CONF-660904, 860
- R. L. Koontz, C. T. Nelson, and L. Baurmash, "Characteristics of Aerosols Generated During Sodium Fires," Transactions of the American Nuclear Society's 1967 Winter Meeting, Chicago, November 5-9, 1967, CONF-671102, 689
- 12. H. A. Morewitz et al., "Sodium Burning, Aerosol Generation, and Control of Fission Product Release During an Accident," Proceedings of the International Conference on the Safety of Fast Reactors, Aix-en-Provence, September 19-22, 1967, Vb-3
- 13. R. L. Koontz, C. T. Nelson, and L. Baurmash, "Modeling Characteristics of Aerosols Generated During LMFBR Accidents," *Proceedings of the Tenth AEC Air Cleaning Conference*, New York City, August 1968 (to be published)
- 14. R. P. Johnson et al., "Characterization of Sodium Pool Fires,"

 Proceedings of the International Conference of Sodium Technology and
 Large Fast Reactor Design, Argonne National Laboratory, November 79, 1968, CONF-681106, ANL-7520, Part I, 195
- "Annual Technical Progress Report, AEC Unclassified Programs, Fiscal Year 1963," NAA-SR-8888

1964," NAA-SR-9999

1965," NAA-SR-11450

1966," NAA-SR-12492

1968," AI-AEC-12721

- 16. E. Garelis, "Sodium-Air Accident Study for a Sodium-Cooled Reactor," AECU-4161 (April 6, 1959)
- P. B. Longton, "Alkali Metal-Gas Reactions Part IX: The Influence of Moisture on the Reaction of Sodium with Oxygen," IGR-TN/C-535 (April 1957)
- P. B. Longton, "Alkali Metal-Gas Reactions Part X: The Influence of Hydrogen on the Reaction of Sodium with Oxygen," IGR-TN/C-536 (April 1957)
- 19. H. Munster, "Investigations of Sodium-Air Reactions," ANL-TRANS-388 (September 1966)
- E. Hines, A. Gemant, and J. K. Kelley, "How Strong Must Reactor Housings be to Contain Na-Air Reactions?," Nucleonics 14, No. 10, 38 (October 1956)
- 21. J. R. Humphreys, Jr., "Sodium-Air Reactions as They Pertain to Reactor Safety and Containment," Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. 11, p. 177 (United Nations, New York)
- L. J. Koch et al., "Hazard Summary Report, Experimental Breeder Reactor II (EBR-II)," ANL-5719 (May 1957)
- 23. I. Charak and F. A. Smith, "Preliminary Evaluation of a Technique to Study Expulsion of Sodium into Air," Proceedings of the Conference on Safety, Fuels, and Core Design in Large Fast Power Reactors, Argonne National Laboratory, October 11-14, 1965, ANL-7120, 868
- 24. N. K. Rumpf, "Pressure Buildup in the Cell and Primary Vault of the FARET from Sodium Fires or Spills," NAA-SR-MEMO-8324 (March 18, 1963)
- 25. F. L. Mangold and R. A. Tidball, "Sodium Fires Studies," NP-3812 (April 23, 1952)
- 26. C. T. Nelson, R. L. Koontz, and M. Silberberg, "Characterization of Sodium Spray Aerosols," Proceedings of the Tenth AEC Air Cleaning Conference, New York City, August 1968 (to be published)
- 27. Cl. Descamps and J. Rygaert, "Behavior of Fission Products in the Atmosphere Surrounding a Sodium-Cooled Fast Reactor Accidental Coolant Fires," Proceedings of the International Conference on the Safety of Fast Reactors, Aix-en-Provence, September 19-22, 1967, Vb-2
- 28. C1. Descamps, "Behavior of Several Fission Products in the Atmosphere Surrounding Sodium-cooled Reactors in the Event of Major Accident," Proceedings of the International Conference of Sodium Technology and Large Fast Reactor Design, Argonne National Laboratory, November 7-9, 1968, CONF-681106, ANL-7520, Part I, 555
- 29. R. D. Keen, "Some Preliminary Experiments with Sodium and Tetralin Fires," NAA-SR-MEMO-1952 (May 31, 1957)
- 30. P. Spiegler et al., "Evaluation of the Equation that Governs the Coagulation of an Aerosol," *Proceedings of the Ninth AEC Air Cleaning Conference*, Boston, September 13-16, 1966, CONF-660904, 626
- 31. P. Spiegler et al., "Characterization of Aerosols Produced by Sodium Fires," NAA-SR-11997 (May 1, 1967)

- 32. D. F. Hausknecht and M. A. Greenfield, "A Model Describing the Behavior of the Aerosol Produced by a Sodium Fires," *Transactions of the American Nuclear Society's 1967 Winter Meeting, Chicago, November 5-9, 1967*, CONF-671102, 690
- 33. R. L. Koontz, C. T. Nelson, and L. Baurmash, "Standardized Generation of Vapor-Produced Sodium Aerosols, and Their Behavior," *Proceedings of the Ninth AEC Air Cleaning Conference*, Boston, September 13-16, 1966, CONF-660904, 848
- 34. H. J. Ettinger, W. D. Moss, and H. Busey, "Characteristics of the Aerosol Produced from Burning Sodium and Plutonium," LA-3491 (July 1, 1966)
- 35. H. J. Ettinger, W. D. Moss, and H. Busey, "Characteristics of the Aerosol Produced from Burning Plutonium," Proceedings of the Ninth AEC Air Cleaning Conference, Boston, September 13-16, 1966, CONF-660904, 905
- 36. H. J. Ettinger, W. D. Moss, and H. Busey, "Characteristics of the Aerosol Produced from Burning Sodium and Plutonium," Nuclear Science and Engineering 30, No. 1, 1 (October 1967)
- H. H. Gott and G. Flook, "The Dounreay Fast Reactor," Engineering, pp 280-2 (August 26, 1966)
- "Final Summary Safeguards Report for the Hallam Nuclear Power Facility," NAA-SR-5700 (April 15, 1961)

4. A Study of Sodium Fires, J. D. Gracie and J. J. Droher, NAA-SR-4383 (summary only)

NAA-SR-4383 REACTORS-GENERAL 90 PAGES

A STUDY OF SODIUM FIRES

By J. D. GRACIE J. J. DROHER

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC. P.O. BOX 309 CANOGA PARK, CALIFORNIA

CONTRACT: AT(11-1)-GEN-8 ISSUED: OCTOBER 15, 1960

II. SUMMARY

The principal reaction products resulting from combustion of sodium are Na₂O (sodium monoxide) and Na₂O₂ (sodium peroxide). In excess sodium the monoxide reaction predominates, while in excess air the peroxide reaction predominates. The combustion reaction is characterized by very low flames and dense clouds of white oxide smoke. Heat must be supplied to start the combustion reaction of sodium at low temperature, but once started, enough heat is liberated to maintain the reaction and gradually raise the temperature of the molten liquid. If the liquid is well insulated thermally, it eventually can increase in temperature to 1630°F, the boiling point of sodium. This is the highest temperature which can be obtained in a pool of sodium under atmospheric pressure. Depending upon the configuration and the resulting heat losses to the surroundings, the pool may attain a much lower equilibrium temperature.

The combustion in air of sodium in a pool proceeds at a rate of about 0.15 to 0.3 lb/min per square foot of exposed surface. The rate tends to increase with pool depth and decrease with surface area. A spray of sodium reacts almost instantaneously.

When sodium is burned, much of the sodium can remain unreacted. Of the sodium that does react, only a small proportion is evolved as smoke. About 4100 to 4850 Btu of heat are liberated for each pound of sodium that burns completely (2280 to 2700 cal/gm). Preliminary tests conducted with gram quantities of radioactive sodium indicate that less than 10% of the initial activity was lost during burning. Therefore, if radioactive sodium is involved in a fire, it should not be assumed that all of the activity is released to the atmosphere. In cleaning the residue after a sodium fire, it should be realized that a large proportion of unreacted sodium may still be present.

Because heat is being generated at the surface of the pool and is being dissipated from the sides and bottom of the pool, a temperature gradient is formed in the pool which decreases with distance from the surface (a typical gradient is 30°F/in.). Above the surface of the pool the temperature decreases rapidly with distance (a typical gradient is 500°F/in.).

The ignition temperature of sodium in air is dependent upon several variables and will be characteristic of the particular system under consideration. The following values may be used as an approximation: Fine particles of sodium condensed from a vapor mist may ignite at room temperature; droplets of sodium sprayed into air may not ignite until about 250°F; a pool of sodium will not ignite until above about 400°F if the surface is distrubed to remove the oxide scum, and above about 550°F if the surface is undisturbed. In some cases, undisturbed sodium has been heated to above 800°F before there was any evidence of ignition.

At oxygen concentrations of 4 vol % and below, sodium at 1000°F did not undergo rapid combustion, as characterized by incandescence; however, a slow reaction, characterized by evolution of some smoke, occurred at oxygen concentrations down to 0.1 vol %. This indicates that a smoke hazard can exist independently of a combustion reaction characterized by incandescence.

Under controlled laboratory conditions and using oxygen under very low humidity conditions (less than 1 grain/lb), the specific type of reactivity is critically dependent upon the partial pressure of water vapor present, and, to a lesser extent, upon the oxygen partial pressure. The moisture content and/or the hydrogen content of a gas surrounding sodium at an elevated temperature can, in certain cases, exert an influence as important as the oxygen content upon the combustion of sodium. Hydrogen influences the reaction of sodium and oxygen in a manner directly comparable to that of water vapor. In the absence of these "catalytic" species, reaction between sodium and oxygen does not occur to a detectable extent even at temperatures up to 1000°F.

If hot sodium is sprayed into an enclosure, heat is transferred from the sodium to the gas in the enclosure, causing a rapid rise in pressure. This pressure rise is accelerated if additional heat is generated by the combustion of sodium. Tests were conducted which showed that the rate of pressure rise increased: (a) as the oxygen concentration was increased from 0 to 5 vol %; (b) as the sodium temperature was increased from 600 to 1200°F; (c) as the moisture content of the gas was increased from less than 3 grains/lb of gas to 300 grains/lb of gas. There was no significant effect of the spraying pressure between 30 and 60 psi. Placing a baffle near the point of leakage of sodium interrupted the spray and resulted in a lower rate of pressure increase than would have been obtained with unobstructed leakage.

A proper understanding of the sodium-water reaction is necessary in evaluating methods of preventing or extinguishing a sodium fire. Water applied to sodium in air will react violently; however, if air is excluded, and if adequate space for expansion is available, the reaction proceeds rather smoothly. If air is not excluded, the hydrogen-oxygen reaction (arising as a result of the hydrogen liberated by the sodium-water reaction) is usually responsible for much of the noise and violence commonly associated with the primary reaction. Reduction of the oxygen content of cover gases to below 5%, in sodium-water systems, prevents explosions between the generated hydrogen and oxygen. It is possible under certain conditions to apply water, in finely divided form and at very low rates, onto sodium in air so that the initial sodium-water reaction proceeds smoothly, and the hydrogen gas which is liberated does not react explosively with oxygen from the air.

The protection of structural members against detrimental effects of sodium, which might leak or spill from a process system, may be accomplished in a number of ways. These ways include: (a) prevention of contact of structural members with leaking sodium, by use of such items as spill pans, equipment enclosures, and vermiculite (expanded mica) insulation, (b) removal of leaking sodium by a vacuum pickup device, (c) pressure control measures to prevent buildup of excessive internal pressures, (d) water control measures to exclude water from a potential spill over, and (e) smoke control measures to remove quickly any caustic fumes which might be evolved.

Many materials are useful in extinguishing sodium fires. Included are Met-L-X, * sodium carbonate, sodium stearate, large-grain vermiculite, G-l foam powder, † lampblack, sand, and calcium carbonate. Liquid hydrocarbon materials also extinguish sodium fires, but a secondary hydrocarbon fire ensues which can be extinguished by application of sodium bicarbonate. At Atomics International, the established method of controlling fires resulting from sodium spills is the shovel application of dry calcium carbonate; Met-L-X (pressurized dry powder) extinguisher units are used to knock down high flames, when necessary for the shovel approach. Replacing the air in a vessel or closed

^{*}A product of Ansul Chemical Co., Marinette, Wisconsin †A product of Pyrene Manufacturing Co., Newark, New Jersey

container with an inert gas will also extinguish a sodium fire by eliminating oxygen. Covering a container of burning sodium will eventually extinguish the fire by oxygen starvation.

Burning sodium can be extinguished rapidly and without mess by a pliable oxygen-excluding blanket. Blankets fabricated from special fabric materials were not capable of withstanding the temperatures encountered during a spill of sodium onto the ground; a blanket of stainless steel foil did perform effectively in such a situation.

The four steps to be followed in combatting a sodium fire are (a) protect yourself, (b) contain the combustibles, (c) extinguish the fire, and (d) clean up.

Most items of personnel protective gear are not able to withstand the <u>continuous</u> effects of burning sodium; however, most of these items are able to withstand the effects of burning sodium for a period of time long enough to permit the wearer either to remove any burning sodium adhering to the protective garments, or leave the area near the burning sodium and then remove the protective garments.

- Extinguishment of Alkali Metal Fires, S. J. Rodgers and W. A. Everson, Fire Research Abstracts and Reviews, 8(1), 40-41 (1966)
- Rodgers, S. J. and Everson, W. A. (MSA Research Corporation, Callery, Pennsylvania) "Extinguishment of Alkali Metal Fires," Fire Technology 1, 103-111 (1965)*

The expanded use of alkali metals as heat-transfer and working fluids has made necessary further investigation of the safety and handling procedures for sodium, potassium, NaK lithium, rubidium, and cesium. The following methods and techniques of extinguishing were evaluated:

- (1) inert gas in the presence of reduced oxygen partial pressures;
- (2) inorganic salts; (3) organic liquids; and (4) foams.

TEC powder, a ternary eutectic compound developed in England, was found to be the most effective inorganic salt extinguishant for sodium, potassium, and NaK fires. Met-L-X was also found to be an effective extinguishant for these fires and may be preferred over TEC because of its lower cost.

For these extinguishants, the weight ratio of extinguishant to alkali metal ranged from 0.72/1 to 0.20/1 depending on the salt used and the size of the fire. For sodium fires up to 500 lb in size, the extinguishing time was of the order of 5 min when the salt was applied from a 350-lb extinguisher. Both TEC and Met-L-X were effective against rubidium and cesium spills, but were ineffective on quiescent pools of these metals. At temperatures of less than 700° F, polyurethane foam was found effective on burning pools of rubidium and cesium. Neither of the above salts was found effective on lithium fires. Graphite is recommended as the extinguishant for lithium fires.

Organic liquids did not prove effective extinguishants. Although they were somewhat effective on low-temperature alkali-metal fires, a secondary liquid fire ensued in all cases. These fires can be severe and troublesome.

Lithium, sodium, and potassium fires were also controlled by gas blanketing and reduction of oxygen partial pressure. At a partial pressure of 0.1 atm of oxygen, none of the above metals ignited, although sodium did emit an occasional spark, and potassium oxidized slowly.

In atmospheres containing 50% argon/50% air, sodium ignited. Lithium and potassium did not ignite although potassium was slowly oxidized. In atmospheres containing 90% argon/10% air, none of the metals ignited. Again, potassium was oxidized slowly.

^{*}Based on Technical Documentary Report No. APL TDR 64-114 prepared by MSA Research Corporation for Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, 1964. Copies of the complete report are available from the Office of Technical Services, U.S. Department of Commerce, Washington 25, D.C.

Rubidium and cesium in quiescent pools exhibited different burning characteristics than sodium, potassium, and lithium. Although 100% of these metals were oxidized in a 90% argon/10% air atmoshpere, there was essentially no smoke, emission of light, or formation of an oxide crust on the surface. Unlike the other alkali metals, the degree of oxidation could not be reduced by altering the atmosphere. Rubidium and cesium did ignite when ejected in a jet stream in a normal atmosphere, but did not ignite in an atmosphere of 50% argon/50% air, 90% argon/10% air, or air of 0.1 atm absolute pressure.

6. Additional References for Appendix C

- Experience with the SIG Nuclear Power Plant, KAPL-1750 (1957).
 (Includes a description of a radioactive sodium fire.)
- Failure of Liquid Metal Pump and Resulting Damage to Pump and Test Facility, The Babcock and Wilcox Co. Report #5040, ES-401-18, NObs-34222, NS643-001, Project "Baby" (Jan 5, 1951).
- 3. C. O. Nelson, Summary Report of Reaction Tests of Various Materials Tested with Sodium and Sodium-Potassium, KAPL-557 (June 1, 1951).
- 4. G. N. Lauben, Initial Experience with Large Sodium Fires Experiments (LF-1), NAA-SR-12041 (Aug 1, 1966).
- S. J. Rodgers and W. A. Everson, Extinguishment of Alkali Metal Fires, MSA Research Corporation, APL-TDR-64-114 or AD-607-978 (Oct 1964).
- R. D. Keen, Some Preliminary Experiments with Sodium and Tetralin Fires, NAA-SR-Memo-1952 (May 31, 1957).
- 7. Liquid-Metal Fire Control, PWAC-347 (June 15, 1961)
- 8. Liquid-Metal Smoke Abatement, PWAC-235 (Nov 1, 1957).
- 9. Marshall Sittig, Safe Handling of Alkali Metals, I & EC 48, 227 (1956).
- Additional Safeguards Information for Hallam Nuclear Power Facility, NAA-SR-5700, Supplement 4.
- 11. A. M. Larsen, Combination Metal and Organic Fires Library Search, NAA-SR-Memo-2010 (July 5, 1957).
- P. Himot, F. J. Viles, Jr., J. Sullivan, and M. W. First, Sodium Aerosol and Its Filtration, 1967 Air Cleaning Conf., Dept. of Industrial Hygiene, Harvard School of Public Health, Boston, Mass. 02115.
- 13. Canel Health and Safety Procedure, Alkali (Liquid) Metal Test Rigs and Experiments, Pratt & Whitney Aircraft, Division of United Aircraft Corporation, Number C5.05 (April 5, 1958).

APPENDIX D

$\frac{\text{Tabular Listing of Known Equipment or Component Failures}}{\text{in Sodium Loops or Reactors}}$

Report		Component	Description		
KAPL-1750, Apr 1, 1957			Experience with the S-1G Nuclear Power Plant, pp. 85-90.		
U.K. Dounreay Ltrs. Sept 18, 19 Dec 4, 1967 Jan 12, 196	7	NaK piping	Crack in weld near pipe stub/vessel nozzle connection.		
MSAR 69-42	p. 5	Plugging valve indicator	Inoperative valve due to ruptured bellows, Dec 2, 1968.		
Apr 1969	p. 7	Stress rod bellows seal	Overextension ruptured bellows causing rise in sodium level and small leakage Oct 26, 1968.		
	pp. 9-12	Bellows sealed valves (4)	Shearing of stems and sticking of plugs due to failure to preheat valve bodies.		
	p. 91	Cover-gas line	Fire in a cover-gas line, no details given (Loop 3).		
KAPL-1450 Nov 1, 1955	pp. 23-33	Tube-to-tube sheet welds	Intergranular NaK in the creep range.		
MSAR 69-7	p. 6	Sealing flange	Sodium leak in flange, Sept 22, 1968.		
Jan 1969		Cover-gas line	High sodium level, Sept 25, 1968, causing a small fire at a leak.		
MSAR 68-14 Jan 1968	p. 11	Sealing flange cover- gas line	Sodium oxide plug in expansion tank caused high-level sodium leak around sealing flanges and into cover-gas line.		
MSAR 66-149 July 1966	p. 24	Plugging indicator valve	Galling of valveno leakage or firevalve replaced.		
MSAR 66-71	p. 15	Bellows seal valve (2 each)	Small sodium leak on outlet valves of two units (ruptured bellows).		
Apr 25, 1966		Main piping damaged	Damaged piping found when insulation was removed, Feb 8-9, 1966.		
MSAR 67-17 eb 3, 1967	p. 7	Bellows seal valves	Repair of several ruptured bellow valves.		
MSAR 66-220	p. 9	Bellows seal valves (2 each)	1. Mainstream bypass valve.		
Oct 1966			Inlet valve to creep rupture test unit.		
MSAR 65-96	p. 4	Bellows seal valve (2 each)			
ug 6, 1965	488	Piping (plugged)	Bellows failure caused temporary shutdown. Bellows and plug replaced, requiring draining of loop.		
			Plug required location and removal. Several plugs encountered in system throughout tests.		
	p. 32	Loop piping	Metallographic examination shows cracks on sodium side of piping.		
ISAR 66-09 an 17, 1966	p. 11	Bellows seal valve	Failure of bellows; sodium leak.		
ISAR 62-126	p. 10	Bellows seal valve	Failure of bellows; sodium leak.		
ct 19, 1962		1/2-in. pipe	Apparently an imperfection in pipe.		
	p. 26	Flange seal	Leak caused by high level in creep pot.		
	p. 28	Bellows seal valve (2 each)	Failure of bellows.		
SAR 66-78	p. 90	Bellows	Failure of numerous bellows seals.		
ay 1966	p. 92	Heater on pipe (2 incidents)	High-temperature oxidation of pipe by heater on 1/2-in. pipe.		
pical Report	p. 92	Plugging of pipes	Sodium plugs that had to be mechanically removed.		
	p. 94	O-ring seals	Flange seals for cover gas. When high sodium levels occurred, sodium leaked through, and eventually caustic residue required replacement of flanges.		
SAR 65-194 c 1965	p. 104	Heating wires on pipe	Required replacement of pipe lines.		
		Bellows seal valves (3 each)	Bellows failures, May 1963.		
oical Report	p. 105	Bellows seal valves (2 each)	Bellows failures, Nov 1963.		
	p. 107	Bellows seal valves	Bellows failure on numerous liquid-metal valves.		
		O-ring seals	Flange seals same as reported above.		
	p. 109	Expansion tank	Improperly placed heaters oxidized through wall of tank.		

Report		Component	Description		
GEAP-5648 July 1968	p. 63	Piping	A sodium leak was a source of nitrogen contamination.		
NAA-SR-12416 Jan-Mar 1967 (A1)	p. 43	Bellows	Three bellows failed during bellows test.		
NAA-SR-12520 Apr-June 1967	p. 55	Bellows	Three bellows failed during bellows test.		
(A1) from BNL 50089 (PR29)		Vol. 5, No. 5, Oct 1967			
Nuclear Metallurgy	p. 233	Thermocouple well	Intergranular cracks caused by carbide precipitation; sodium leaked into well.		
/ol. IX 1963	p. 243	Tee	Cracks caused by temperature gradients in the tee. Mixing of hot and cold streams of sodium, $ \\$		
Alkali Metals Coolants Nov 28-Dec 2	p. 231	Bellows failure	Interaction or infusion of Na at grain boundaries.		
ORNL-3955	p. 70	Sodium cooler (A1)	Failure in Feb 1963. Program terminated in June 1963.		
Vol. 1		AEC Contract AT (11-1) Gen 8-4468			
	p. 196	Pipe (minutes of Sept 1960 meeting)	GE loop No. 5; small leak badly corroded outside of pipe.		
	p. 200	Small sodium leaks in duPont equipment (minutes of Sept 1960)			
	p. 211	Flanged joint	GE small leak that erroded away much outside surface (minutes of Nov 1960).		
	p. 221	Pipes (minutes of Mar 16, 1961)	GE Loop No. 5; small leaks causing rapid erosion or corrosion of outside of pipes.		
	p. 273	Valve body (minutes of Mar 1962)	Warpage of body during thermal shock tests. Body removed and remachined; LCTL. $ \begin{tabular}{ll} \hline \end{tabular} \begin{tabular}{ll} \end{tabular} $		
	p. 299	Na to air cooler (minutes of Oct 1962) (side-shell heat transfer)	Intergranular corrosion, Oct 10 (A1).		
ORNL-3955 Vol. 2	p. 481	Bellow seal valves (meeting Feb 1965)	Failure of bellows due to poor valve design and carburization.		
Investigation of physical properties		OCI valves and pump	Plugging of valves and pump.		
of materials in hi-temp. Na		Test units inlet and outlets	Plugging of lines.		
		Expansion tank	Leaks in tank walls, caused by poor positioning of external heaters.		
	p. 483	Test unit inlet and outlet, valve, and the cold trap	Plugging and general plating.		
GE Na mass transfer program	p. 501	Mechanical joints Conoseal joints	Failure of joints responsible for majority of sodium leaks.		
		Loops 1 and 3-6	Fouling-flow reduction caused by deposit products.		
		Pump cells (1961)	Tubing failure resulting in a sizable sodium leak.		
ORNL-3955 /ol. 3	p. 599 p. 1083	Loop 5 Sodium cooler	Two major sodium leaks in newly installed equipment. Main sodium cooler developed leaks and was replaced; shellside heat transfer		
	p. 1141	1/2-in. Schedule 40 pipe	(A1) SCDP, Oct 1962. During flange repair, Apr 1963, pipe broke in two. GE Loop No. 1 mass transfer.		
	p. 1152	Bellows seal valve	Bellows leak on startup. GE Loop 4, May 1963.		
	p. 1152 p. 1163	Valve	Improperly seated valve caused a leak, damaging wiring on insulation. MSA, June 1963.		
	p. 1165	Sample holder	Leak at H3R sample holder, June 1963. GE Loop 2 mass transfer.		
	p. 1205	Sodium pumps	EBR-II pumps failed, Oct 1963. Improper heat treatment of shafts.		
		Sodium pumps	HNPF primary pumps failed. Bearing misalignment and metal particles.		
		Sodium pumps	HNPF pump; presence of sodium on shafts prevented restart after a scram.		
	p. 1225	Sodium pumps	EBR-II pumps removed from primary tank. M-1, pump case off center and pun shaft was bent. M-2, pump shaft rubbing against lower labyrinth, Dec 1963.		
	p. 1231	Pump cell	Failure of pump cell, GE, mass transfer, Jan 1964.		

Report		Component	Description
ORNL-3955	p. 1231	Fuel gripper	Failure due to oxide buildup, Jan 1964, EBR-II.
Vol. 3 (Contd.)	p. 1232	Sodium pump check valve	No. 1 primary pump Enrico Fermi Atomic Power Plant. Replaced check valve, Jan 1964.
	p. 1239	Sodium pump	HNPF leak on upper pump seal No. 1 primary pump, Feb 1964.
	p. 1255	Pump duct	EBR-II Apr 15, 1964; Cracks 2-3 in. long.
	p. 1255	Valve bellows	HNPF valve in primary sodium service cell, Apr 1964.
	p. 1284	Valve bellows	Outer ply of 2-ply bellows in contact with sodium disintegrated during removal. Brittle pieces. (MSA) Aug 1964.
		Bellows seal	Leak in seal Aug 21, 1964.
	p. 1286	Piping	Failure due to trace heater arc to pipe; sodium leaked. Aug 16, 1964 (MSA).
		Bellows valve	Bellows on inlet valve Unit No. 6, Aug 15, 1964.
	p. 1288	Thermocouple well	EBR-II, Aug 9, 1964. Sodium leakage into well, shorting out thermocouples.
	p. 1296	Main fuel gripper	Damaged due to misalignment from heat distortion.
	p. 1307	Expansion tank	HNPF Oct 18, 1964; sodium leak at junction of pump overflow line and X-tank.
	p. 1317	X-tank	Further discussion of leak.
	p. 1360	Valve packings	Sodium leakage at valve packing, Apr 1965.
	p. 1367	Bellows seal valves (3)	SCTL-AI Bellows Failure (May 1965).
			1. Crack in a convolution.
			Leakage resulted in 100-lb sodium spill. All bellows valves to be replaced t freeze stems.
CONF-650411 NEC-NASA iquid Metals	p. 123	NaK heater tube	Failure of heater-tube sigma-phase embrittlement, followed by thermal shock. SNAP-8 NAK Program.
nformation Neeting Npr 23, 1965			
VCONF 28/P/312 May 1964		Piping and heaters	Electric heaters shorting out to piping and burning holes in wall causing sodium leaks.
NNL letter May 28, 1969, to R. Singer from C. D. Claar		Pipe 304 SS	Sodium leakage occurred where pipe failed due to longitudinal cracks which propagated from sharp-cornered machined grooves in OD of the pipe.
ibliography on Liquid Metals Technology		Argon inlet line	Two sodium fires occurred. A plug formed in the inlet line. Attributed to localized O contamination (from KAPL-337).
eport No. 2550 of Hg, , Na, and NaK, ept 1963,	pp. 2-49	Bellows	Bellows failure in bellows tests (from MSA NP-6220, <u>Test of Proposed Design S1G Bellows in Na</u> , Memo Report 100 by Kennedy, Dec 22, <u>1955</u>).
erojet-General	pp. 2-70	Heat exchanger	Failure of two Type 347 SS tubes (NaK outside mercury inside) and two tube- sheets. Cracks caused by thermal cycling. (KAPL-M-WLF-5)
	pp. 2-97	Flange	Failure of outlet flange stud and incipient bearing failure. (AD 277379-GE)
	pp. 3-87	Sodium still	Two fires in sodium still. (KAPL-337)
	pp. 4-37	Liquid-metal pump	Byron-Jackson Pump under test failed, and the NaK leakage caused a fire. Failure caused by one of the ball bearings breaking and piercing the SS liner. (NP-3380, Failure of Liquid Metal Pump and Resulting Damage to Pump and Test Facility) Jan 5, 1951.
	pp. 6-27	E-M pumps	An Investigation of E-M Pump Failures, KAPL-M-JJM-1.

APPENDIX E

Safe Handling of Alkali Metals

 A Primer for the Safe Use of Liquid Alkali Metals, Frank A. Anderson, ORNL-TM-1740

ORNL-TM-1740

Contract No. W-7405-eng-26

REACTOR DIVISION

A PRIMER FOR THE SAFE USE OF LIQUID ALKALI METALS

Frank A. Anderson

JANUARY 1967

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

CONTENTS

	Page
Preface	1
Introduction	1
Properties of the Alkali Metals	3
Physical Properties	3
Color	3
Electrical Conductivity	4
Thermal Conductivity	4
Specific Gravity	4
Melting Point	5
Softness	5
Chemical Properties	5
Reactions with Oxygen	5
Reaction with Water	8
Reaction with Steam	9
Reaction with Carbon Tetrachloride	9
Reactions with Alcohols	10
Inertness to Noble Gases and Nitrogen	11
Design of Liquid Alkali Metal Experimental Facilities	11
Experimental Apparatus	11
Driptrays	11 12
Shields	12
Drain Tanks	12
Cover Gas	13
Cold Traps	13
Air and Water Lines	14
Storage Facilities	14
Handling of Alkali Metals	15
Protective Clothing	16
General Safety Precautions	16
Elimination and Disposal of Residual and Waste Alkali Metals	17
Fighting Alkali Metal Fires	19
First Aid	22
Summary	23
Bibliography	24

1

A PRIMER FOR THE SAFE USE OF LIQUID ALKALI METALS

Frank A. Anderson

PREFACE

The increasing interest in and use of the so-called "liquid metals," especially in nuclear energy applications, has resulted in the gradual development during the past 25 years of a considerable body of knowledge dealing with the characteristics of these materials and the techniques for their safe handling. To make pertinent bits of this information available to the engineers, scientists, and technicians who are concerned with the use of liquid metals, this primer has been prepared. Primary emphasis is placed on providing a background of information that will give the newcomer a sound, meaningful, and working insight into this field of interest, or, in simple words, to give him a "feel" for the subject. The primer is actually what the name suggests. It is not intended to be a chemical treatise or a detailed design or instruction booklet.

INTRODUCTION

The 100-plus elements that make up all matter may be loosely divided into two groups, the metals and the normetals. Most of the metals are solids at or near normal room temperatures, have a silvery appearance (gold and copper are well-known exceptions), and are conductors of electricity. Although mercury is the best known liquid metal, several other metals also exist in the liquid state at or near room temperatures. Examples, with their melting points, are cesium (83°F), gallium (86°F), and rubidium (102°F). Other metals that have relatively low melting points include potassium (146°F), sodium (208°F), indium (311°F), and lithium (354°F). Mixtures, or alloys, of sodium and potassium, usually designated by the combined chemical symbols NaK (pronounced "nack"), may have melting points as low as 10°F. A multicomponent alloy (sodium-potassium-cesium) has been developed recently that is reported to have a melting point of -110°F. 1

Five of these liquid or near-liquid elements have similar chemical properties and are known as the <u>alkali metals</u>: cesium (Cs), rubidium (Rb), potassium (K), sodium (Na), and lithium (Li). These metals, plus their many low-melting-point alloys such as NaK, are now often referred to loosely as the "liquid metals." It is these metals and alloys that are of basic interest to us in this primer.

The steady growth of interest in the alkali metals during the past two decades is due almost solely to the pressing needs of the nation's nuclear energy and aerospace programs. In particular, the requirement for high-temperature coolants has focused attention on several interesting characteristics of the alkali metals: (a) their long liquidus range (see Table 1), (b) their low vapor pressure at high temperatures, (c) their stability (since they are elements), (d) their low specific gravity, (e) their excellent heat-transfer characteristics, and (f) their compatibility, when free of impurities, with many of the "solid" metals and their alloys.

Table 1. Selected Physical Properties of the Alkali Metals

Metal	Cesium	Rubidium	Potassium	Sodium	Lithium
Melting point, °F	83	102	146	308	354
Boiling point, °F	1260	1270	1400	1618	2440
Liquidus range, °F	1177	1168	1254	1410	2086
Specific gravity	1.873	1.532	0.859	0.972	0.534

As is usually the case in most matters, a price must be paid to gain the advantages of the alkali metals. These metals have several undesirable properties that must always be borne in mind and given major consideration by the equipment designer and the user. The alkali metals are extremely reactive (cesium is considered the most chemically active of all the metals), reacting readily with oxygen, water, carbon dioxide, many organic materials, and a number of materials of construction. These chemical characteristics obviously impose stringent, even severe, limitations on the use and handling of the alkali metals and their alloys. Despite these limitations, however, experience has shown that the alkali metals can

be used profitably and safely. A sound, basic understanding of the nature of these metals and a healthy respect for their properties—based on understanding and not fear—will help prepare newcomers to this field to design sound, safe equipment and to handle liquid metals with efficiency and safety.

Succeeding portions of this primer are devoted to brief discussions of the important characteristics of the alkali metals, to general suggestions concerning basic design features of liquid metal facilities, and to recommendations for the safe handling and use of these metals. Suggestions and recommendations reflect the general status of the art, not specific procedures or practices followed by certain research institutes, universities, governmental agencies, or industrial establishments. For specific recommendations pertaining to the various Oak Ridge facilities of the U. S. Atomic Energy Commission, the reader is urged to read the Alkali Metals Safety Guide, Report No. Y-811, Supplemental Issue of May 15, 1961.²

PROPERTIES OF THE ALKALI METALS

Only those properties of the alkali metals and their alloys that are of general concern and importance in the design of liquid metal facilities and in the use and handling of liquid metals are covered in this section of the primer.

Physical Properties

The alkali metals have many physical properties in common. They all have a silvery color in the free, unoxidized state (cesium is an exception, having a gold color), are good conductors of electricity and heat, have low specific gravities (or densities) for metals (see Table 1), have low melting and high boiling points (see Table 1), and are soft and easily worked in the solid state.

Color

Pure samples of alkali metals should have a clean metallic luster and silvery color (with the exception of cesium). If this is not the case, the metal is either oxidized (see section on Chemical Properties) or is otherwise contaminated.

Electrical Conductivity

The electrical conductivity of the alkali metals is good and may be used to advantage (a) by employing electromagnetic meters to determine the rates of flow of the molten metals through pipelines, (b) by employing electromagnetic pumps to pump molten alkali metals, and (c) by utilizing electrically operated liquid level devices to sense the level of liquid metals in storage tanks and surge pots.

Thermal Conductivity

The alkali metals, like most metals, are good conductors of heat—a property that accounts for many of the uses of these substances.

Sodium has a thermal conductivity comparable to nickel and almost twice that of potassium. Both of these metals have conductivities that are considerably higher than that of their various NaK alloys. NaK is peculiar in that its conductivity does not vary greatly with temperature. Sodium and potassium show a marked decrease in thermal conductivity with increasing temperatures.

Specific Gravity

The light weight (low specific gravity or density) of the liquid alkali metals has the advantage of reducing the total weight of liquid metal systems and also makes it easy to transfer liquid metals by pressurizing (with an inert gas such as nitrogen, helium, or argon) or "blowing." The light weight also means that lithium, sodium, and potassium will tend to float on water, on most aqueous solutions, and on some organic liquids. It is important that this fact be considered when plans are formulated for fighting alkali metals fires. A smothering agent, for instance, to be effective in quenching such a fire, should either float on, or be capable of forming a product that will float on, the molten metal.

Boiling Point

The high boiling points of the liquid alkali metals, in comparison to the boiling points of organic liquids, mean that the vapor pressures of these materials will be low at most temperatures of current interest.

Even at temperatures as high as 1800°F, for example, almost 200°F above

its normal boiling point, sodium has a vapor pressure less than 3 atmospheres. Most liquid alkali metal systems, therefore, are low pressure systems, an obvious advantage in design.

Melting Point

As low as the melting points of the liquid alkali metals are, they are above normal room temperatures (with the exception of cesium and some NaK alloys). This means that freezing of the metal will occur if temperatures in liquid alkali metal systems drop too low, and plugging of the system or parts thereof will eventually take place. This possibility must especially be guarded against in instrument lines and in other system branches in which flow does not normally occur. At the same time, an advantage exists in that "freeze-seal" techniques can be used as necessary to seal off or to block liquid metal systems.

Softness

The solid alkali metals are soft enough so that they can be cut with relative ease with a knife. This softness, combined with the low melting points of the metals, is advantageous when disassembling equipment that has been incompletely drained.

Chemical Properties

Because of the similar electronic structure of the atoms of the alkali metals, each atom having one electron in its outer shell or orbit, the chemical properties of these metals are very similar. In general, differences in the chemical properties from one alkali metal to the next represent gradual transitions rather than abrupt changes. Thus, specific knowledge of the chemistry of any one alkali metal provides general knowledge of the chemistry of all these metals. One highly important property characterizes the alkali metals—their extreme reactivity. The alkali atoms lose their single outer electrons readily. In other words, they are easily oxidized and thus are good reducing agents.

Reactions with Oxygen

If M represents an atom of any alkali metal, the following simplified equation may be used to show one typical reaction of the metal with oxygen:

(1)

Depending on the particular alkali metal involved and other factors such as the temperature and whether or not the oxygen is dry or moist, the reaction may proceed slowly and almost imperceptably or rapidly and brilliantly. Sodium, for instance, reacts readily with the oxygen of the air at room temperature to form a thick coating of the white oxide but will not ignite spontaneously until its temperature is about 115°C (239°F), or about 30°F above its melting point. Liquid NaK formulations, on the other hand, may ignite spontaneously in the atmosphere at room temperatures. The heat released by the reaction of a solid alkali metal can raise the temperature of the body and ultimately melt it. As the temperature rises, the reaction increases in speed until finally the metal ignites and begins to burn, producing large volumes of a thick, white smoke, composed of the oxide (M20) combustion product. Not all of the oxide is carried away as smoke, however; much of it remains behind at the combustion site. Because no flammable vapors are produced, as is the case when wood, coal, oil, and other organic materials burn, the burning alkali metal does not produce typical combustion flames. Flames, if there are any, are small, and may not be readily visible. A brilliant light may be emitted from intense "hot spots," which are the combustion sites or areas. In the case of sodium, the hot spot of burning metal is a brilliant yellow. Once a mass of sodium has ignited, for example, the temperature of the liquid pool of metal will build up gradually and may reach as high as the boiling point (1618°F). Rubidium and cesium, the less well-known and less used alkali metals, apparently do not behave entirely like sodium on combustion. 3 According to Rogers and Everson 3 "... burning characteristics of the metals (alkali) are a function of (their) oxide solubility "

Although the voluminous white smoke produced from the burning alkali metal looks threatening, there is no danger of explosion from the burning metal itself. The white smoke, however, is dangerous, because the hot oxide particles are very reactive and will readily combine with moisture in the air, or on the skin, or from any other source.

$$M_2O + H_2O \rightarrow 2MOH \tag{2}$$

The alkali hydroxide, MOH, is a strong caustic that will "burn" skin, eyes, and other tissue. Lung tissue can be severely damaged by this and other caustic material. Obviously, therefore, personnel who are fighting an alkali metal fire or who are in the vicinity of a fire should minimize exposure to the smoke. Nature has provided a protective mechanism in that the fumes normally cause discomfort to eyes, skin, and nose well before overexposure or excessive concentrations occur. However, protective clothing and breathing apparatus should be used by personnel who fight these fires unless the fires are very small and not likely to spread.

Both alkali oxides (M₂0) and hydroxides (MOH) are powerful corrosives and will attack tissue, clothing, and many materials of construction. Because these substances are readily soluble in water, washing affected areas with <u>large</u> volumes of water is immediately beneficial. <u>Large</u> volumes of water must be used to keep the concentration of the resulting hydroxide solution so low that the solution will not cause trouble.

Although the alkali metals will ignite spontaneously when heated in the atmosphere, it has been reported that they can be heated to their melting points in an atmosphere of <u>dry</u> oxygen without reaction. Once the metal is molten, spontaneous ignition soon follows in most instances. Ignition may occur over a significant temperature range, depending on the specific metal involved, the humidity of the surrounding atmosphere, the nature of the surface, the amount of material present and its degree of dispersion, and the oxygen concentration of the surrounding atmosphere. Sodium, for example, will not burn in an atmosphere containing less than about 5% oxygen, although it may continue to react and to produce some smoke. Excluding oxygen, therefore, is the basis for one method of fighting alkali metal, as well as other, fires.

Although the chemical properties of the alkali metals are similar, as previously stated, there are differences that should be recognized. Whereas

sodium reacts with oxygen of the air to form the oxide, Na₂O, potassium reacts to form the peroxide:

$$2K + O_2 + K_2O_2$$
 (3)

This peroxide, under certain circumstances, can react explosively with organic material. As a general safety precaution, thus, it is good practice to keep the alkali metals away from organic materials.

Reaction with Water

The alkali metals react violently with water, usually with an accompanying explosion caused by the secondary reaction of the liberated hydrogen with the oxygen of the air.

$$2M + 2H2O + 2MOH + H2 + Heat$$
 (4)

$$2H_2 + O_2 + 2H_2O$$
 (5)

The heat liberated by reaction (4) is sufficient to cause reaction (5) to occur. When explosion occurs, the unreacted metal is usually scattered over a wide area, where it can cause further trouble. In view of the foregoing, it is a cardinal rule when handling the alkali metals to keep them completely isolated from water or aqueous solutions. This means, too, when fighting alkali metal fires that water or water solution fire extinguishing agents such as the soda-acid-foam types must never be used.

It is interesting to note that investigators at Mine Safety Appliances Company, Callery, Pennsylvania, have shown that sodium can be disposed of safely under water by forcing the molten metal (at 350°F) through an "open end" annulus at Reynold's numbers over 45,000 provided a minimum water depth of 10 ft. is used.

Reaction with Steam

Although water and steam are identical so far as chemical composition is concerned, steam does not necessarily react with the alkali metals with the same physical effect as does water. The hydrogen resulting from the

reaction is often sufficiently diluted so that the danger of an explosive reaction with oxygen from the air is greatly minimized. Dry steam (steam free of condensed water), therefore, is extensively used to clean apparatus or piping containing sodium. The steam not only dilutes the by-product hydrogen but also helps to exclude oxygen from the reaction site and to dissipate the heat of the reaction. To increase further the safety of this operation, an inert diluant gas such as nitrogen or argon might be mixed with the steam. It goes without saying, however, that the steam cleaning of apparatus, especially when restricted passages are involved, must always be carried out with the exercise of due precautions, for even though no chemical explosion might occur, by-product hydrogen might accumulate and build up enough pressure to fracture explosively the unit being cleaned.

Reaction with Carbon Dioxide

The reactions of the alkali metals and carbon dioxide are complex but probably can be simply and adequately summarized as follows:

$$2M + CO_2 + M_2O + CO$$
 (6)

$$M_2O + CO_2 + M_2CO_3$$
 (7)

Principally because of reaction (6), it is not advisable to use carbon dioxide as an extinguishant on alkali metal fires. Reaction (6) produces not only the highly caustic oxide, M_2O , but also poisonous carbon monoxide, CO. The formation and accumulation of CO in a laboratory or in a closed environment raises the possibility of asphyxiation of operating or firefighting personnel who might be trying to extinguish an alkali metal fire with CO_2 .

Reaction with Carbon Tetrachloride

The reaction of the alkali metals with carbon tetrachloride (CCl₄) and other halogenated hydrocarbon (i.e., trichloroethylene) is characterized as being of explosive violence. Consequently, it is considered sound design practice to isolate completely the alkali metals from these materials. Furthermore, there is the possibility that deadly phosgene

gas can form when CCl, is used on an alkali metal fire. Thus, carbon tetrachloride or the familiar Pyrene-type of fire extinguishants are forbidden for use on alkali metal fires.

Reactions with Alcohols

The alkali metals will react with alcohols in basically the same manner as they react with water, but the reaction proceeds more slowly.

$$M + ROH + ROM + 1/2 H_2$$
 (8)

("R" represents an organic radical such as CH3 (methyl), C2H5 (ethyl), C3H7 (propyl), C4H9 (butyl), etc.) By using a large volume of alcohol with a small amount of metal, the reaction can be controlled to provide a safe means for the disposal of waste alkali metals. Care must be taken, of course, because both hydrogen and heat are produced by the reaction; and the alcohols themselves are flammable. In general, the rate of the reaction decreases as the molecular weight of the alcohol increases. Thus, for instance, the reaction will be markedly slower with butyl alcohol (butanol-CuHqOH) than with ethyl alcohol (ethanol-CyHqOH). Because the chemical activity of the alkali metals increases with increasing atomic weight, it is advisable, when disposing of waste alkali metals, to use the higher weight alcohols with the higher weight metals. It is also known that NaK alloys react more vigorously with a given alcohol than does sodium. If therefore a given amount of a certain alcohol is known to give a smooth, safe reaction with sodium, it would be advisable to use a greater amount of a heavier (i.e., higher molecular weight) alcohol for reaction with NaK.

Since the alcohol-alkali metal reaction is controllable, alcohols are often used to free intricate apparatus or equipment from alkali metals. Precautions should be taken to make certain that the hydrogen released by the reaction does not accumulate and build up a potentially dangerous pressure. The ROM compounds, or alcoholates, formed by the alcohol-alkali metal reaction are not considered as corrosive as the alkali hydroxides (ROH). Thus they are not as dangerous to handle. They are corrosive, however, and should be handled with respect and care,

as should all chemicals. If splashed on the skin and clothing, they should be washed off immediately.

Inertness to Noble Gases and Nitrogen

The alkali metals, reactive as they are, will <u>not</u> react with nitrogen (see comment about lithium that follows) or with any of the elements collectively known as the "noble gases"—helium (He), neon (Ne), argon (A), krypton (Kr), and xenon (Xe). Hence, the readily available and inexpensive nitrogen gas and the two most readily available and least expensive noble gases, helium and argon, are often used as "cover" gases to exclude oxygen from the alkali metals. At the higher temperatures, helium and argon are most commonly used since nitrogen may react with the solid, metallic components of a system to form nitrides that alter the physical properties of the system piping, tanks, and other components. At high temperatures nitrogen will also react with lithium to form lithium nitride, thus introducing a contaminant in a liquid lithium system.

DESIGN OF LIQUID ALKALI METAL EXPERIMENTAL FACILITIES

The design considerations and recommendations made herein are based on experiences gained from the design and operation of liquid alkali metal facilities by numerous investigators over the past 20 years or more. Reasonable adherence to the suggestions that follow should result in the design of facilities that are safe to use and easy to operate.

Experimental Apparatus

In general, the comments that follow apply to laboratory bench-scale apparatus and larger, pilot-plant facilities.

Driptrays

Use driptrays under all apparatus and equipment. If leakage or equipment failure should occur, the tray will confine the molten alkali metal to the experimental area and make fire fighting easier. The protection so afforded concrete floors will help to prevent explosive spalling of the concrete. Spalling of concrete in direct contact with burning alkali metals could send showers of the molten metal over operating and firefighting personnel and over adjacent areas, thus enhancing the possibility

of damage resulting from a fire. Although driptrays are extremely useful, it should be noted that the oxides formed during an alkali metal fire may migrate over the walls of a tray. This oxide possesses a "wicking" action that can draw liquid metal over the edge of the tray and thus drain metal from the tray. (For further information, see reference 3.)

Perforated flooring for driptrays having a maximum open area of about 25 per cent have been shown to be effective in limiting the access of air to burning alkali metal, thus serving to extinguish the fire.

Driptrays are also useful in helping to confine fire-fighting chemicals and thus to improve their effectiveness.

Shields

Use metal shields that are fitted inside the lip of the driptray around all liquid metal containing apparatus and equipment. If leakage or failure does occur, the shields will minimize the danger to operating personnel from the spraying liquid metal and will help to confine the metal to the driptrays.

Hood s

Locate experimental and test apparatus under a hood when possible. Hoods can prevent the spread of the irritating white oxide particles from an alkali metal fire. The copious clouds of smoke may be dense enough to limit vision in the area of an alkali metal fire and to hinder operation of equipment, providing first aid, and fighting the fire. However, the hood must not discharge into an area where the oxide smoke could cause more trouble than if it were confined to the general area of the fire. High ceilings and overhead forced ventilation can serve as an adequate substitute for hoods.

Drain Tanks

Include dump, sump, or drain tanks at a low point in the liquid metal system. In an emergency, it will often be possible to dump much of the liquid metal in an apparatus or system, thus minimizing the spill and, consequently, minimizing fires and the problem of cleanup after a fire. Drain tanks should be large enough to hold more than the entire volume of liquid metal in a system. The design of the system should be such that it will drain completely by gravity. The pressure of a cover gas (see next

section) may be of use in draining a system more rapidly than can be achieved by gravity alone. However, one may have to forego this advantage and release or decrease the pressure in the event of an emergency to cut down the loss of molten metal through system leaks.

Cover Gas

Use an inert cover gas in the liquid metal system. By using an inert gas such as nitrogen, helium, or argon under pressure in the liquid metal system, several advantages will be gained: (a) pressure will be available to help dump the liquid metal in the event of an emergency, and (b) the inleakage of air to the system will be minimized. Minimizing the oxygen in a liquid alkali metal system will reduce the amount of alkali metal oxide formed and help to keep the system clean. These oxides have a limited solubility that is markedly temperature dependent -- the solubility decreasing with decreasing temperatures. Troublesome deposits of oxides, therefore, will accumulate in the cold portions of a liquid metal system and may lead to plugging of lines. Every possible precaution should be taken to minimize oxide formation for a second reason: The oxides contribute to corrosive attack on many materials of construction, thus inviting trouble and lessening the life expectancy of the liquid metal system. Because nitrogen will react with hot lithium to form lithium nitride, thus introducing an impurity into a lithium system, nitrogen is not recommended as a cover gas for lithium.

Cold Traps

Include a "cold trap" in the liquid metal system. As pointed out in the preceding section, alkali metal oxides show decreasing solubilities with decreasing temperatures. This property can be used to advantage to help keep liquid alkali metals clean by the installation of "cold traps" or "cold fingers." The cold trap is normally a tank containing a mesh packing, through which the liquid metal is pumped and cooled. Precipitated oxides are retained on the packing. Cold fingers are nothing more than small vessels on stubs of piping that are incorporated in the colder portion of the liquid alkali metal system. By keeping the cold finger markedly colder than any other part of the system, alkali oxides will gradually accumulate by diffusion in the trap, thus helping to keep the

system clean and free of troublesome deposits. Cold trap design is an art rather than a science and should be learned from experimenters who have had successful experience with the operation of these devices. It must be remembered that whether planned or not, the coldest point in any alkali metal system will automatically function as a cold trap.

Air and Water Lines

Do not use air or water lines in conjunction with piping handling liquid metals without serious consideration of the safety aspects involved. When designing and installing liquid metals systems, never make it possible—directly or indirectly through cross connections—to introduce air or water into any piping through which liquid metals will flow. In preceding sections of this primer, the danger involved in mixing air and water with alkali metals has been pointed out repeatedly.

Storage Facilities

It is a good rule to assume that all chemicals are dangerous in one way or another and that thought and care must be given to their safe use, handling, and storage. In view of the reactive nature of the alkali metals, it should be evident that special consideration must be given to the specific problem of the storage of the alkali metals. The bibliography of this primer contains several references to articles on this subject.

Commercial-grade alkali metals are normally received from the producer in the form of bricks, which are stacked in airtight metal containers having readily removable covers. High purity alkali metals and alloys (NaK) are usually shipped in metal containers equipped with valves, so that the liquid can be forced from the container by inert gas pressure.

Containers should always be stored on cement blocks or platforms (do not use wooden supports) above the floor level to facilitate visual inspection of the container for leakage and to prevent liquid spills of any kind on the floor from coming into contact with the containers. The storage area should <u>not</u> contain a sprinkler system and should <u>not</u> have water lines passing through it. It is important also that the area be kept free of other materials that might react with spilled or leaking alkali metal or that, if a fire started, would require the use of

extinguishants that might react with the alkali metals. All organic materials, including wooden shipping containers and boxes and paper, should be kept out of the storage room. It is highly recommended that the room or area in which alkali metals are stored be used for this purpose only.

The storage area should be posted with signs (including "No Smoking") indicating the nature of the stored material and warning against the use of water or other fire extinguishants that will react with the alkali metals. A supply of the proper type of fire extinguishing material should be nearby. If these materials are capable of absorbing moisture, provision must be made to keep them dry. The storage area must be kept dry and should be well ventilated to keep the humidity at a minimum and to remove the heavy oxide fumes if a fire should start.

HANDLING OF ALKALI METALS

Alkali metals can be handled safely and with a minimum of danger if they are given the consideration that they deserve and require. It is the responsibility of the individual who is directly concerned with the handling and use of alkali metals to acquire a sound, basic understanding of the nature of these useful—and reactive—materials, so that he may approach the problem of handling them with confidence. The key to the safe use of all materials is to "know them."

It is not within the scope of this primer to provide step-by-step directions for handling alkali metals under specific conditions. Instead, suggestions and recommendations are advanced which, upon study, will provide the reader with information—based on the chemical and physical properties of the alkali metals—to enable him to develop the all-important "feel" for this problem. With this "feel," or background of stored information, the reader will be in a position, with experience, to develop his own safe procedures or directions for handling specific problems involving the alkali metals.

It is recommended strongly that at least two persons be involved in any situation where alkali metals are being handled or used. This excellent safety precaution cannot afford to be relaxed. If one person should panic

or become incapacitated in the event of an accident, the second person can be available to take over or to provide help. This second person is also available, if necessary, to start fire fighting, to help shut down equipment, to turn in an alarm, or to provide any other assistance that might be needed.

Protective Clothing

Before anyone becomes involved in a problem dealing with the handling of the alkali metals, the type and the location of the available protective clothing and equipment should be determined. Protection should be available for the head, face, eyes, hands, body, feet, as well as for the breathing passages and the lungs. Remember that ordinary cotton or synthetic fiber clothing offers little or no protection against the liquid alkali metals except at room temperature. According to information released by the Mine Safety Appliances Company, 5 chrome leather gloves and aprons and laminated Bakelite hats offer 100% protection against 500°C (932°F) sodium and NaK. Rubber gloves, face shields with acetate windows and MSA Nu-Looks goggles protect against 150°C (302°F) NaK and 350°C (662°F) sodium. MSA chipping goggles and MSA welding goggles show excellent resistance. It is unreasonable to expect this clothing to withstand prolonged or severe exposure to molten or burning alkali metals. For instance, no protective clothing or equipment currently available can withstand the effect of a 1/16-in.-diam stream of lithium at 600°C (1100°F) and 60 lb per in.2 (Ref. 3). Specific information on protective clothing is found in TRG Report 25C, "Guidance in the Safe Handling of Alkali Metals." published in 1961 by the United Kingdom Atomic Energy Authority and in the report prepared by Rodgers and Everson. 3

General Safety Precautions

The following general safety precautions should be observed at all times when handling the alkali metals.

1. Do not smoke. Make certain also that there are no open flames of any kind in the area.

- Make certain that an adequate supply of fire controlling and extinguishing material is on hand to deal with any spillage or fire.
- 3. Make certain that all equipment, including tools, to be used during the handling operation is absolutely dry. The use of nonsparking tools in opening alkali metal drums is strongly recommended since hydrogen can accumulate in the drums and cause explosion and fire. If moisture from the air were trapped in the container from a previous opening, it would have reacted with the alkali metal to produce hydrogen. Although it may appear unlikely that a dangerous amount of hydrogen will be formed in this manner, it should be assumed that this could happen.
- 4. If a "hissing" sound is heard when an alkali metal container is opened, hydrogen gas may be present in a dangerous amount. Proper ventilation in the area will help to disperse the hydrogen and will lessen the danger of an explosion.
- Handle solid alkali metals only with tongs or with nonporous, washable gloves.
- 6. Transfer all molten alkali metals at the lowest possible temperature and pressure to minimize the possibility of fire or the effect of an accident.
- Always use an inert cover gas when transferring molten alkali metals.
- 8. Be prepared to remove promptly any spilled alkali metals or residues from alkali metal fires.
- 9. Replace drum covers immediately after removing alkali metal bricks to minimize the introduction of oxygen and moisture. By replacing the drum covers, the possibility of a future accident will be lessened and contamination of the metal (by the formation of oxides, hydroxides, and carbonates) kept to a minimum.

Elimination and Disposal of Residual and Waste Alkali Metals

Sooner or later the investigator working with NaK or an alkali metal will face an important problem: How do I eliminate or dispose of waste or residual material? Suggestions for dealing with this eventuality are presented herewith.

If a waste disposal officer is a member of your organization, waste disposal plans should first be discussed with him, particularly if sizable amounts of waste are involved. If a special waste disposal facility exists, it is probable that skilled personnel will assume the responsibility for disposing of accumulated waste metal. The waste disposal suggestions that follow, thus, deal primarily with the problem of collecting and disposing of small amounts of waste alkali metals.

- 1. In the case of a spill, shovel the liquid material into a dry, metal container equipped with a lid and replace the lid promptly. This procedure may be followed even if the metal is burning. With the lid in place, oxygen will be excluded; and the fire will go out. If preferred, a suitable fire extinguishant (possibly powdered graphite or Met-L-X Powder) can first be showeled or sprayed on the spill before the metal is put into the disposal container. A layer of the extinguishant may also be added to the container before the spilled or waste metal is dumped therein.
- 2. Small amounts of waste or residual metal in small sections of piping or tubing or in small pieces of apparatus can be eliminated by placing the unit in a container of alcohol of the proper kind (see Section "Reactions with Alcohols" p. 10). When the reaction between the alkali metal and the alcohol is over (make certain no unreacted alkali metal remains in the liquid), dispose of the resulting solution through a laboratory sink drain. Flushing of the sink with a large amount of water is then advisable.
- 3. When NaK or other liquid metals are drained from a sizable piece of equipment, residual metal may remain throughout the equipment due to poor drainage, low spots, or crevices. In cases such as this, a suitable alcohol (see Section "Reactions with Alcohols" p. 10) may be circulated through the system to remove the alkali metal, making certain that the system is kept open so that the by-product hydrogen is allowed to escape safely.

Dry steam may also be used effectively to clean apparatus. The apparatus should first be heated (trace heating is entirely suitable) to above 100°C to prevent condensation of steam. Care should be taken to make certain that no air enters the system with the dry steam. In an air-free atmosphere, the steam-alkali metal reaction will proceed smoothly without

danger of an explosion. A final flush with water is normally permissible after other cleaning techniques have been applied. If the mixture leaving the apparatus being cleaned contains the strongly caustic alkali hydroxide formed by the reaction, the mixture should not be discharged indiscriminately.

Fighting Alkali Metal Fires

If a person handling or using an alkali metal always remembers that a fire might occur--but that the fire can be handled safely if he knows the ground rules--he will always be psychologically prepared if a fire should break out. He should remember that flames, if any, may be practically invisible, that large quantities of white, opaque smoke will be produced, but that the burning metal cannot, of itself, explode. An alkali metal fire, as such, is not particularly hazardous (all fires, of course, present a hazard) but secondary effects--the caustic alkali oxide cloud of smoke and reactions with nearby materials--may be.

In his excellent article "Extinguishing Sodium-Potassium Alloy Fires," Lee⁷ points out that, as with regular fires, three ingredients are necessary before it is possible to have a fire: fuel, heat, and oxygen. Removal of any one of the three ingredients will extinguish the fire.

Under ordinary conditions, if a fire develops, first remove the alkali metal fuel. Although this removal will not extinguish the fire, it will limit the size of the fire. If only a small amount of metal is involved, the simplest and safest procedure may be to do nothing—simply allow the metal to burn and keep a safe distance away from the smoke. Under certain conditions, it may be advisable to leave the scene of the fire temporarily to turn in a fire alarm.

When larger amounts of alkali metal, several pounds or more, are burning, a standard procedure for handling the fire should be put into operation. This means that no one should handle or use alkali metals without first developing, or becoming familiar with, an emergency procedure that is applicable to his particular situation.

Heat is the second ingredient necessary for a fire. Although "cooling" a fire will lessen its intensity, or even extinguish it, this is not always easy to accomplish. Since this procedure is normally not applicable to alkali metal fires, it will not be discussed here.

Oxygen is the third ingredient necessary for an alkali metal fire. If oxygen is excluded, the fire promptly dies out; for, in every sense of the word, it suffocates. Actually, a nonflammable, nontoxic, and nonreactive liquid having a high latent heat and producing a heavy (high molecular weight) vapor would be an ideal fire fighting material. If such a liquid were sprayed on a fire, vaporization would absorb the heat, thereby cooling the fire and helping to extinguish it. Furthermore, as the heavy vapor formed, it would blanket the fire and exclude oxygen, thus extinguishing the fire. Unfortunately, no such ideal fire fighting liquid exists. Fire fighting materials that are used, therefore, have limitations that make them suitable only for rather specific purposes. It is not too surprising, consequently, that the well-known fire extinguishants such as carbon dioxide, carbon tetrachloride, and water are not suitable for use on alkali metal fires. A review of the chemistry of the alkali metals presented in the section on "Chemical Properties," p. 5 will show why these materials should never be used to combat alkali metal fires.

Several fire fighting materials that are recommended for use on alkali metal fires are discussed briefly below:

1. Soda Ash (anhydrous Na_2CO_3). Only the anhydrous and completely moisture-free material is suitable for use. This substance can be sprinkled or shovelled on the fire or sprayed on from an extinguisher, using CO_2 pressure. The powder blankets the fire and tends to prevent the reaction of the carrier gas (CO_2) with the metal. Soda ash is often used on sodium fires and is generally accepted as being suitable for use on potassium and NaK fires. A General Electric safety manual 8 states

that "Soda ash is not recommended as an extinguishing agent for lithium since it reacts violently on contact."

- 2. Zirconium Carbonate. (See general comments under "Soda Ash"). This material has been used effectively on alkali metal fires. It is expensive, though, in comparison to soda ash and does not appear to have specific advantages that make its use compelling.
- 3. Powdered Graphite. This is an excellent blanketing agent and has been widely used in fighting alkali metal and NaK fires. Care should be taken to distribute the graphite powder smoothly over the burning metal and to avoid dumping it on the fire. Dumping might cause splattering of the burning metal and might also result in the mass of graphite sinking through the burning metal, thus failing to provide the desired blanketing effect. Rodgers and Everson³ report that graphite is the best among many extinguishants tested on lithium fires. The action of graphite on a liquid metal fire is apparently dual. By blanketing the surface, the powder excludes air, thus suffocating the fire. Also, since it is a respectable conductor of heat, the graphite probably cools the burning metal somewhat and thus helps to extinguish the fire.
- 4. Met-L-X. This fire fighting material is a dry, free-flowing, impregnated sodium chloride (distributed by Ansul Chemical Company), which is available in pressurized extinguishers. When Met-L-X is sprayed on an alkali metal fire, it forms a crust that excludes oxygen from the fire-thus extinguishing it. It is usually considered advisable to intermittently sprinkle the Met-L-X lightly on the burning surface. This procedure will hasten the formation of the crust. Met-L-X is not combustible and thus will not cause secondary fires when it is used on liquid metal fires. Because of its ability to adhere to molten sodium, Met-L-X is particularly suitable for use on sodium fires on walls and piping. It is advisable to clean thoroughly the high-temperature equipment in the area where Met-L-X has been used to avoid corrosion problems in subsequent operation.
- 5. Pyrene G-1 Powder. This material is a graphite-base extinguishant produced by the Fyr-Fyter Company. It may be applied from tubes, or, if it is available in bulk form, may be sprinkled from shovels. Since it is not combustible, secondary fires will not result from its application to a burning alkali metal.

Details concerning the performance of various materials tested for their ability to extinguish burning alkali metals and NaK may be found in the report prepared by Rodgers and Everson, ³ pp. 36-37. An excellent analysis of fire extinguishants is made by Gracie and Droher ⁹ in Chapter V of their exhaustive report entitled "A Study of Sodium Fires."

First Aid

Personnel handling or using alkali metals should know the basic rules of first aid, so that effective action can be taken and help administered should an accident occur. An amply supplied first aid cabinet or locker located nearby in a readily accessible area is basic to providing aid. Minimum first aid material should include tongs or tweezers, some kind of a scraper or spatula, swabs, bandages, and a container of mineral oil. Tongs are useful in picking chunks of metal from clothing or skin. A scraper or swab is useful in scraping alkali metal from clothing and skin. Mineral oil can be used to cover a cleaned area to exclude air and moisture from residual material.

If an accident occurs and someone is splashed with molten alkali metal that is not burning, the metal should be scraped from the skin as rapidly as possible. Should the metal have come in contact with normal work clothing, the clothing should be removed promptly, the alkali metal in contact with the skin swiftly scraped off, and the affected areas flooded with mineral oil. Any detectable bits of alkali metal should be removed promptly with the tweezers or by swabbing. The accident victim should then be removed to a hospital or infirmary for observation by trained medical personnel and for any further treatment that is necessary.

If a person has been sprayed with burning alkali metal, the same general procedure as outlined above may be followed or an alternate procedure used. This alternate procedure calls for immediate removal of all clothing and massive amounts of alkali metal, flooding of the affected areas with large amounts of water (small amounts will probably do more harm than good), and neutralizing with a 3% acetic acid solution. According to the Liquid Metals Handbook, 10 considerable controversy exists concerning the best procedure to be followed in giving first aid to a person splashed with burning liquid metal.

It is suggested, therefore, that the reader determine what the recommended procedure is at his laboratory or installation and that he act accordingly in the event of an emergency.

Although prompt first air treatment is always in order, it is a necessity in the case of an eye burn. If goggles did not provide protection and an eye is burned, it should be flooded immediately with large amounts of low pressure water for about 15 minutes. The eye should then be treated with a 5% solution of boric acid to neutralize any caustic that may still remain. Subsequent treatment by medical personnel is always recommended even though no apparent damage may have been suffered.

SUMMARY

The liquid alkali metals are valuable but are very reactive and potentially dangerous materials. With a sound understanding of, and an appreciation for, their characteristic physical properties and chemical nature, they can be used profitably and with safety. It is the responsibility of the individual who needs to handle and to use the alkali metals and their alloys to acquaint himself with the pertinent information concerning these materials so that he can proceed with their use with confidence.

Bibliography

- F. Tepper, J. King, and J. Greer, Multicomponent Alkali Metal Alloys, MSA Research Corporation Report AFAPL-TR-65-73, July 1965.
- 2. P. L. Hill, Alkali Metals Area Safety Guide, Carbide and Carbon Chemicals Company, Oak Ridge, Tennessee, August 13, 1951. Supplemental Issue May 15, 1961 (Report Y-811).
- S. J. Rodgers, and W. A. Everson, Extinguishment of Alkali Metal Fires, Technical Documentary Report No. APL-TDR 64-114, Air Force Aero Propulsion Laboratory (Wright-Patterson Air Force Base, Ohio), October 1964, pp. 28-31.
- R. C. Andrews, and E. C. King, Underwater Disposal of Molten Sodium,
 Mine Safety Appliances Company Technical Report 29, July 30, 1954.
- 5. L. F. Little, Action of NaK and Na at Elevated Temperatures on Protective Material, Mine Safety Appliances Company Report 1 (Contract NObs 45468), November 10, 1948.
- 6. A. Thorley, and A. C. Raine, Guidance in the Safe Handling of Alkali
 Metals, United Kingdom Atomic Energy Authority TRG Report 25(C), 1961.
- 7. R. F. Lee, Extinguishing Sodium-Potassium Alloy Fires, Callery Chemical Company Report SP-119, September 14, 1954.
- Space Power and Propulsion Safety Manual, Missile and Space Division,
 General Electric Company, Cincinnati, Ohio, (June 1964).
- 9. J. D. Gracie and J. J. Droher, A Study of Sodium Fires, NAA-SR-Y383, October 15, 1960.
- 10. C. B. Jackson, Liquid Metal Handbook (Sodium-NaK Supplement), Atomic Energy Commission, Department of the Navy Report TID-5277, p.392, July 1, 1955.
- 11. D. B. Nelson, Guide to Liquid Metal Handling, Knolls Atomic Power Laboratory, USAEC Report AECU-1273, March 1, 1951.

2. Methods Used by an AEC Contractor for Handling Sodium, NaK and Lithium

Accident and FIRE PREVENTION information United States Atomic Energy Commission

ISSUE NO. 110

February 16, 1960

METHODS USED BY AN AEC CONTRACTOR FOR HANDLING SODIUM, Nak AND LITHIUM

An AEC contractor has furnished us with data and information concerning his methods of purchasing, storing, handling, using and disposing of alkali metals. He writes as follows:

"Pursuant to your request, the following data and information are furnished concerning the purchase, storage, handling, use and disposal of alkali metals. Following is a list of such metals currently in use on this project, with pertinent data.

Metals	Symbol	Melting Point	Weight per Gal.
		•	
Sodium	Na	207°F	8.2 lbs.
Sodium-potassium	NaK	70°F*	7.5 lbs.
Lithium	Li	354°F	4.5 lbs.

"The following is a summary of the detailed procedures for handling each alkali metal.

"Sodium - Sodium is purchased and received in steel 55-gallon drums, being in the solid state as received. Until required for use, it is stored in the liquid metal storage building on the site. When required for use, one drum at a time is transported to the batch-down area adjacent to the test location. The drum is placed in a thermostatically-controlled drum heater, blanketed with argon gas, and brought to a molten state. By application of gas pressure, the metal is forced into a container on a mobile transfer dolly specifically set up for Sodium. This dolly includes heat equipment and insulation around the container, as well as an argon gas supply for blanketing and

^{*}Complete solution.

156

ISSUE NO. 110

pressure transfer. When filling of a rig is required, the dolly is taken to the test rig location and an argon gas cover system, controllable from the control panel of the dolly, is tied into the loop to be filled. The loop is then brought up to temperature corresponding with the liquid metal temperature. By regulating gas pressure from the control panel, the liquid metal is forced into the test apparatus to the proper levels as determined by probes.

"When tests are terminated, the sodium is removed from the test apparatus by a reversal of the fill process. The apparatus is then allowed to cool down and any residual Sodium freezes in place. After the test unit has been cut apart, the various sections are sent to a building for decontamination. In the case of Sodium, the parts are immersed in a tank of alcohol, and the resulting chemical reaction removes any solid Sodium. When all chemical reaction ceases, the parts are then transferred to a separate area where they may be safely sprayed with live steam under pressure. This is a precautionary measure to remove minor quantities of Sodium and/or oxides which might be entrapped in seams or crevices.

"To dispose of larger quantities of contaminated Sodium, it would be melted as described above and transferred into disposal pans in the burn pit, ignited and burned to complete destruction.

"Due to the low original cost of Sodium, there is no economical feasibility in attempting to reclaim it.

"Sodium-Potassium - The Sodium-potassium alkali liquid metal combination commonly referred to as NaK, is currently purchased in 30 or 55-gallon reinforced stainless steel drums. These are the property of the project, and empty drums are returned to the supplier for refilling and reshipment to us. Although NaK has to be above 70°F to be in complete solution, it is in liquid solution at all normal atmospheric temperatures and is, therefore, normally considered and handled in the liquid state. Here again the normal practice is for all material not in use or awaiting use to be stored in the liquid metal storage building.

"When a quantity is required for filling a rig, a drum is moved to the batch-down area and placed in a drum heater and brought up to 250°F to insure that the Sodium is in complete solution. During this period the drum is blanketed with argon, and argon gas is also bubbled through the NaK to provide a mixing action. The drum of NaK is then placed on a transfer dolly and transported to the test rig area. The rig itself is heated if necessary to be sure that all parts of the rig are above 70°F, and the transfer is made as indicated for Sodium above, utilizing argon gas pressure to effect the transfer.

"Since many of our NaK rigs involve larger quantities, it is current practice to recover used NaK and save it for other tests. This is accomplished at the conclusion of the test by permitting the rig to drain into the sump tank and then removing it from the sump tank by a reversal of the fill process. By filtration through a 10 micron filter, NaK may be reused for additional tests.

"Because NaK remains in liquid form at all normal atmospheric temperatures, it is essential that test apparatus be completely drained, and argon gas pressure is utilized to assist in the complete removal. As the test apparatus is cut apart, special attention is given to the possibility that small quantities may still be trapped in various components, and each of these is carefully handled. As many cuts are made as are necessary to insure that all liquid quantities can be drained. If a residual quantity is found in a component, this is poured into a pre-dried disposal container on to a layer of Met-L-X powder and held for disposal. Components are then flushed with live steam to remove any residual quantities that might be trapped in seams or cracks that may have developed in welds. Small quantities of NaK referred to above, which were drained into disposal containers, are placed in a destruction area where a fine water mist may be directed upon the containers. This causes rapid oxidation or burning to take place, and is continued until all of the metal is consumed. This procedure is only used for small quantities, usually not in excess of 2 lbs.

"When a quantity of NaK is contaminated beyond further use, it is disposed of by transferring it as described into disposal pans in the burn pit and safely burned. It is interesting to note that the destruction of classified aluminum printing plates is accomplished under AEC supervision during the burning of contaminated NaK.

"Lithium - Lithium is currently purchased in 30-gallon reinforced stainless steel drums which are reusable. Because of its melting point, Lithium is received and stored as a solid. Because our current tests require less than one pound per filling, slightly different procedure is used here than in the cases described above. The drum of Lithium is placed in a batch-down area in the Lab, where it is heated to a molten condition under a gas blanket of argon. A small quantity, approximately 1-1/2 lbs., is then transferred into a portable fill tank containing titanium sponge as a 'getter.' During this filling operation, periodic samples are taken by inserting an oversized sampling tube in the fill line. After the filling has been completed and the Lithium allowed to freeze again, this sample tube is forwarded to the Lab for analysis as a continuing check on the purity of Lithium. A similar sampling tube is inserted in the fill line from the fill tank to each test rig,

ISSUE NO. 110

158

February 16, 1960

and is again forwarded to the Lab for determination of the purity of the metal actually used in each test. A quantity of these fill tanks are kept on hand at all times. These are kept at room temperature with the Lithium in a solid state and with an argon gas cover to prevent contamination. When a quantity is required for filling a test rig, one of the fill tanks is installed on a specially designed transfer dolly inside of a thermostatically controlled heater. Again the gas cover system and pressure control for both the fill tank and the test rig are controlled from the panel of the transfer dolly. For purification purposes the metal is brought up to 1600°F, held for 2 hours, then dropped to 1000°F and the transfer effected under

isothermal conditions to prevent damage due to thermal shock.

"Because of the small quantity involved, no attempt is made to recover Lithium after test. When a test is complete, the apparatus is allowed to cool at room temperature, and the Lithium solidifies. The test apparatus is then cut up and sent to the appropriate building for decontamination. The individual components are immersed in a tank of water and allowed to remain there until the resulting chemical reaction completely disintegrates and removes all of the metallic Lithium. When this is complete, the components are again finished off with live steam under pressure to remove any residual entrapped quantities.

"As indicated above, we do not currently have a problem of disposing of large quantities of Lithium. Should this ever be necessary they would be melted and transferred to pans in the burn pit, then ignited and burned to destruction."

Safety and Fire Protection Branch Office of Health and Safety U.S. Atomic Energy Commission Washington 25, D.C. 3. Explosions Involving Metallic Potassium or NaK

information United States Atomic Energy Commission

ISSUE NO. 251

March 13, 1967

EXPLOSIONS INVOLVING METALLIC POTASSIUM OR NaK

Like the other alkali metals, potassium reacts with water or moisture to form hydrogen which may explode when mixed with air and ignited. Also, like other alkali metals, potassium can react readily with air to form oxides which present a hazard because of their caustic properties. However, the residue obtained by the air oxidation of potassium is of particular concern since it presents an added hazard due to the frequent presence of K_2O_4 (potassium superoxide), a powerful oxidant capable of exploding when in contact with unreacted potassium, alcohol, kerosene and many other flammable materials.

The attached (reproduced, with permission, from United Kingdom Atomic Energy Authority Safeguards Bulletin, Issue 2/66) covers a series of incidents attesting to the extent to which the "normal" potassium handling hazards may be increased by the presence of superoxides formed by prior reaction of the metal with air.

Division of Operational Safety U.S. Atomic Energy Commission Washington, D.C. 20545

March 13, 1967

ISSUE NO. 251

SODIUM POTASSIUM ALLOY EXPLOSIONS

Over the last few years there have been reports of many incidents in which personnel have been injured by explosions during the handling of potassium or sodium - potassium alloys. Reproduced below is a summary of these incidents and comments on the mechanism of the reaction and recommendations for the handling of NaK or K residues.

Incident No. 1 (Reported in greater detail in Safeguards Bulletin 2/63)

In 1962 an Australian research laboratory experienced a serious explosion during the handling of waste sodium potassium alloy. About 100 gallons of NaK were being transferred from transport containers to a tank through a pipeline equipped with filters to remove grit, oxides etc. Periodically the filters were opened and the cake clogging the filter scraped into a drum. At the time of the accident a waste drum was placed beneath the open filter and the filter cake removal commenced. Liquid NaK began to drop, it was unquestionably hot and there was evidence that some drops were burning. A few seconds after this process began, the explosion occurred.

The Committee of Inquiry concluded that the essential component of the explosive mixture could only be potassium superoxide.

Incident No. 2 (Board of Enquiry held 22.10.63)

At AERE two operators were dismantling and cleaning rigs (Argon driers) which were known to be contaminated inside with traces of NaK. The equipment consisted of two stainless steel pots interconnected with $\frac{3}{8}$ " I.D. stainless steel tubing. The pot lids were flanged and secured with four bolts and sealed with a P.V.C. gasket.

The normal procedure is to remove the bolts, withdraw the lid and pipework and to lower the pot into a water tank. The lids and pipework are cleaned in a similar manner.

Two dustbins, containing four assemblies immersed in oil were removed from the sodium store. Two of the assemblies were dealt with without incident, but the lid of one pot of the third assembly was stuck and could not be easily removed. The first operator attempted to prise the lid from the pot with the head of the spanner but was unsuccessful and the second operator left the scene to obtain a screwdriver and hammer. At this point an explosion occurred. The pot was later found in the water tank and the pipework about ten feet away.

ISSUE NO. 251 March 13, 1967

The first operator was convinced that at the moment of the explosion he was not banging, scraping or doing anything which may have produced a spark or frictional heat.

The Board of Enquiry concluded that the explosion was probably caused by reaction between potassium tetroxide and oil but a hydrogen/oxygen explosion could not be completely ruled out.

Incident No. 3 (Private communication to Safety Manager DERE)

At King's College London, a pot of NaK had been used for gas purification of argon (removal of oxygen, hydrogen and water) and after completion of the experiment the pot and contents were set aside. Several months later an explosion occurred when a laboratory attendant poked a hole through the crust which had formed on the top of the NaK.

Incident No. 4 (Reported in Safeguards Bulletin 1/64)

To dispose of a piece of NaK oxide crud, the material was placed in an open steel capsule and then into a glove box. The box was purged with argon for ten minutes and than about 10 ml of alcohol was added to the crud. There was an immediate rise in pressure causing the glove to burst and a flame issued from the port causing superficial burns to the operator.

Incident No. 5 (Chemical and Engineering News, Vol. 26, No. 36)

(September 6, 1948, Page 2605)

2,000 pounds of potassium bricks which had been stored for several years were found to be covered with a layer of potassium superoxide (potassium tetroxide) (K_2O_4) which varied in thickness from 0.25 to 0.5 inch. During an attempt to break off the scale, some of the potassium tetroxide was driven into the underlying metal and a violent explosion occurred.

Incident No. 6 (Quarterly Safety Summary, 1965, Vol. 36, Page 2, No. 141)

A piece of potassium metal, about 2 cc in size, had been taken from the stock bottle, placed on two thicknesses of clean dry filter paper and blotted dry.

The metal was then sliced with the stainless steel blade of a pocket knife. After several cuts had been made, the residual lump of potassium suddenly exploded and inflamed, small particles of the burning metal being scattered over the bench surface and on the clothing, hands and face of the operator. Safety spectacles prevented any eye injury.

March 13, 1967

ISSUE NO. 251

Incident No. 7 (Chemistry and Industry, February 20, 1965, Page 353)

A young assistant was asked to dispose of the contents of a bottle which had contained potassium, but from which the protecting liquid had long evaporated. The metal had been in the form of spheres 8 or 10 mm in diameter but had been completely converted into a white substance which the assistant assumed to be potassium carbonate. He cut one of the spheres in half and it appeared to be quite homogeneous, but thinking there might be some unreacted metal left be dropped the half sphere (say about 0.5 g) into an evaporating dish of aqueous alcohol. There was a violant explosion and the dish was shattered.

 $\frac{\text{Incident No. 8}}{\text{Explosion at DERE}} \left(\begin{array}{c} \text{Report of the Technical Investigation Committee on a NaK} \\ \end{array} \right.$

At an A.E.A. site in 1956-57 some contaminated NaK was transferred from a rig to two oil type drums of about two gallons capacity.

In 1963 when preparing the NaK for disposal it was found that the closure caps on the oil drums could not be removed and a hole was punched in the top of each drum and the liquid contents transferred to the standard type of container.

In March 1966 all three drums were transferred to D.E.R.E. At the disposal booth one of the oil drums was emptied without incident. In the case of the second oil drum the (pierced) closure cap appeared to have been tightened on a crossed thread. To release it, the chargehand tapped the cap several times with a hammer and a violent explosion occurred, showering the man with burning NaK. His protective clothing saved him from serious injury.

Mechanism of the Explosion

It is concluded that the above explosions were caused by the formation of potassium superoxide (potassium tetroxide, $\rm K_2O_4)$ due to long exposure of the NaK or potassium to air and that the potassium superoxide reacted explosively with liquid metal and/or organic material.

Recommendations

1. Since prolonged storage of NaK residues in contact with air leads to the formation of potassium superoxide, all efforts should be made to follow the practice of immediate disposal of residues.

ISSUE NO. 251 March 13, 1967

2. There should be no inter-establishment transfer of NaK suspected to contain potassium superoxide.

- 3. Where there are any grounds for suspecting that formation of potassium superoxide has taken place, handling of the NaK and containers should be done remotely. No attempt should ever be made to open suspect containers other than by remote operation and the contents should also be disposed under remote conditions. Movement of the containers (inside the establishment) to the place of disposal should be effected as gently as possible lifting should be done by crane and adequate provision for shielding made on the transporting vehicle, for example, sandbags.
- 4. In the event of a situation arising where it becomes necessary to store NaK residues, then the residues should be stored in dry air-tight containers under an atmosphere of inert gas. Addition of an oil seal should be avoided, since an explosive reaction could take place between the oil and superoxide, or the oil, superoxide and NaK.

In U.K.A.E.A. establishments potassium is normally handled in small quantities but the explosive power of relatively small pieces of oxidised potassium is well illustrated in the above recorded incidents and, in addition, the formation of potassium superoxide takes place more readily than in the case of NaK. In view of this behaviour it is essential to ensure that oxidation of even small amounts of potassium should not take place. Laboratory stocks are normally kept under an oil seal and it is important that the potassium should not be allowed to protrude above the oil surface. Further to this it is reported by $\operatorname{Sax}^{(1)}$ that the superoxide can form even under mineral oil, therefore, stocks of potassium should be kept under periodical review and appropriate disposal action taken if the presence of superoxide is detected.

(The above summary and recommendations have been extracted from a document originally produced by the Safety Manager, D.E.R.E.)

⁽¹⁾ SAX, N.I. - Dangerous Properties of Industrial Materials - Reinhold Publishing Corp., New York.

4. Additional References for Appendix E

- Liquid Metals Handbook, Sodium and NaK Supplement, Chapter 18, Safety (June 30, 1967).
- Guide to Liquid Metal Handling, Liquid Metals Safety Committee,
 D. B. Nelson, Chairman, AECU-1273 (Mar 1, 1951).
- A. Thorley and A. C. Raine, Guidance in the Safe Handling of Alkali Metals, TRG Report 25(c), UKAEA (1961).
- 4. Sodium, Data Sheet D-231 (Revised), National Safety Council, 425 North Michigan Avenue, Chicago, Illinois 60611.
- 5. W. W. Kendall, L. H. B. Peer, W. J. Scheiber, and F. C. Steiner, Guide to Alkali Metals Handling, Liquid Metals Safety Committee Manual, LMSC-1, AECU-3143 (July 1, 1954).
- 6. P. L. Hill, Alkali Metals Area Safety Guide, Y-811 (Aug 13, 1951).
- 7. M. Sittig, Safe Handling of Alkali Metals, I&EC 48, p. 227 (1956).
- 8. Properties and Essential Information for Safe Handling and Use of Sodium-Sodium Metal-Metallic Sodium, Chemical Safety Data Sheet SD-47 (1952), Manufacturing Chemists' Association, Inc.
- 9. Canel Health and Safety Procedure, Number C5.05, Alkali (Liquid) Metal Test Rigs and Experiments (Apr 7, 1958), Pratt and Whitney Aircraft, Division of United Aircraft Corporation.
- 10. J. W. Mausteller, F. Tepper, and S. J. Rodgers, *Alkali Metal Handling* and Systems Operating Techniques, Published by Gordon and Breach, New York, 1967 (ANS-USAEC Monograph).
- 11. Handling Metallic Sodium on a Plant Scale, U.S. Industrial Chemicals Company, 99 Park Avenue, New York, N.Y., 3rd Ed. (1959).

ACKNOWLEDGMENTS

We wish to acknowledge the help and excellent cooperation of the ANL staff and management personnel. Personnel at the Liquid Metal Engineering Center and Mr. L. E. Oldendorf, AEC-CH Safety and Technical Services Division, supplied the Committee with valuable information on sodium fires and related subjects. Valuable comments on a draft copy of this report were received from Mr. R. B. Smith, Fire Protection Engineer, Division of Operational Safety, AEC Headquarters. We also wish to gratefully acknowledge:

- 1. The UKAEA for permission to include in Appendix B an unpublished paper by A. W. Smith and J. L. Drummond.
- 2. The Oak Ridge National Laboratory (N. T. Bray) for permission to include in Appendix B a report by F. A. Anderson.
- 3. The North American Rockwell Corporation (Atomics International Company--O. G. Jenkins, A. E. Miller, and J. J. Droher) for permission to include one report in Appendix B and three reports in Appendix C.
- 4. The Ansul Company (M. R. Kraus) for permission to include in Appendix B three of their reports on extinguishing agents for metal fires.

REFERENCES

- J. D. Stearns (private communication); also, R. K. Wagner and J. D. Stearns, "Evaluation of Non Fuel Material Behavior in HNPF," in Proceedings of Sodium Components Development Program, Chicago, June 16-17, 1965, CONF-650620.
- 2. A. S. Meyer, Jr., and J. P. Young, "Detection of Traces of NaK in Air," in Aircraft Nuclear Propulsion Project Quarterly Progress Report for Period Ending March 31, 1957, ORNL-2274, p. 137.
- 3. A. S. Meyer, Jr., and J. P. Young, "Detection of Traces of NaK in Air," in Aircraft Nuclear Propulsion Project Quarterly Progress Report for Period Ending June 30, 1957, ORNL-2340, Parts 1-5, p. 166.
- 4. A. E. Wechsler, Characteristics of Metal Vapor, ARL 66-0004, Arthur D. Little, Inc. (Jan 1966).
- A. E. Wechsler, P. E. Glaser, and J. Jasperse, Characteristics of Metal Vapors, ARL-65-53, Arthur D. Little, Inc. (Mar 1965).
- 6. A. E. Wechsler and P. E. Glaser, Radiation Characteristics of Metal Vapors, ARL-63-37, Arthur D. Little, Inc. (Feb 1963).
- 7. J. A. Fassel and D. W. Golightly, Detection Limits of Elements in the Spectra of Pre-mixed Oxy-Acetylene Flames, Anal. Chem. 39, 466-476 (1967).
- 8. R. E. MacPherson, Sodium Burning and Aerosol Release--An Evaluation of the State of the Art, ORNL-TM-1937 (May 6, 1968).
- 9. T. S. Krolikowski, Violently Sprayed Sodium-Air Reaction in an Enclosed Volume, ANL-7472 (Sept 1968).
- 10. J. D. Gracie and J. J. Droher, A Study of Sodium Fires, NAA-SR 4383 (Oct 15, 1960).
- S. J. Rodgers and W. A. Everson, Extinguishment of Alkali Metal Fires, MSA Research Corporation, APL-TDR-64-114 or AD-607-978 (Oct 1964).
- 12. Underwriters' Laboratories Fire Protection Equipment List, pp. 56 and 57 (Jan 1969).
- M. E. Remley, private communication, Atomics International, North American Rockwell Company (Nov 10, 1970).
- 14. R. D. Keen, Some Preliminary Experiments with Sodium and Tetralin Fires, NAA-SR-Memo-1952 (May 1957).
- 15. C. O. Nelson, Summary Report of Reaction Tests of Various Materials
 Tested with Sodium and Sodium-Potassium, KAPL-557 (June 1, 1951).
- L. Baker, Jr., and A. D. Tevebaugh, "Sodium-Air Reaction Calculations," in Chemical Engineering Division Semiannual Report, January-June 1965, ANL-7055, pp. 208-211 (Oct 1965).